Tris(guanidinato)complexes of iridium and rhodium in the oxidation states +III and +IV: synthesis, characterization, and reactivity

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TRIS(GUANIDINATO) COMPLEXES OF IRIDIUM AND RHODIUM IN THE
OXIDATION STATES +III AND +IV: SYNTHESIS, CHARACTERIZATION, AND
REACTIVITY

by
Wei-Tsung Lee

An Abstract
Of a thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

December 2011

Thesis Supervisor: Assistant Professor Jan-Uwe Rohde
ABSTRACT

Mononuclear \([\text{Ir}\{\text{ArNC(NR}_2\text{NAr}\}\} (\text{C}_8\text{H}_{14})_2]\) complexes (where \(R = \text{Me} \) or \(\text{Et}\); \(\text{Ar} = \text{Ph}\) or \(4\)-MeC\(_6\)H\(_4\); and \(\text{C}_8\text{H}_{14} = \text{cis}-\text{cyclooctene}\)) were synthesized from the neutral \(N,N\)-dialkyl-\(N',N''\)-diarylguanidines via deprotonation and transmetalation. As confirmed by single-crystal structure determination, the guanidinato\((1−)\) ligands coordinate the low-valent d\(^8\) \(\text{Ir}^1\) center in an \(N,N'\)-chelating binding mode, and the C–N distances of the CN\(_3\) core suggest that these ligands function as stronger donors than related monoanionic, bidentate nitrogen-based ligands. In the reaction of the complexes with \(\text{O}_2\), new \([\text{Ir}\{\text{ArNC(NR}_2\text{NAr}\}\}_3]\) complexes were identified among the products, suggesting a new route for their synthesis.

Tris(guanidinato) complexes of \(\text{Ir}^{\text{III}}\), \([\text{Ir}\{\text{ArNC(NR}_2\text{NAr}\}_3]\) (\(R = \text{Me} \) or \(\text{Et}\); \(\text{Ar} = \text{Ph} \) or \(4\)-MeC\(_6\)H\(_4\)), were synthesized and, as revealed by electrochemical measurements, can be oxidized reversibly at unusually low potentials. These potentials are even lower than those of other \(\text{Ir}^{\text{III}}\) complexes with very electron-rich, trianonic ligand sets as, for example, in cyclometalated tris(2-pyridylphenyl), corrolato and tris(dithiocarbamato) complexes. Chemical oxidation by \([\text{FeCp}_2]\text{PF}_6\) afforded isolable, paramagnetic \(\text{Ir}^{\text{IV}}\) compounds, \([\text{Ir}\{\text{ArNC(NR}_2\text{NAr}\}_3]\text{PF}_6\), which were characterized by elemental analysis, mass spectrometry, electronic absorption and EPR spectroscopy and X-ray crystallography. The reactivity of these \(\text{Ir}^{\text{IV}}\) complexes toward mild inorganic and organic reductants and substrates with O–H bonds was investigated.

Similar tris(guanidinato) complexes of \(\text{Rh}^{\text{III}}\), \([\text{Rh}\{\text{ArNC(NR}_2\text{NAr}\}_3]\) (\(R = \text{Me} \) or \(\text{Et}\); \(\text{Ar} = \text{Ph} \), \(4\)-MeC\(_6\)H\(_4\) or \(4\)-MeOC\(_6\)H\(_4\)), were synthesized. These complexes also were oxidized reversibly at low potentials, as compared to the corresponding tris(amidinato) and tris(triazenido) complexes. Chemical oxidation by \([\text{FeCp}_2]\text{PF}_6\) afforded thermally unstable, paramagnetic \(\text{Rh}^{\text{IV}}\) compounds, \([\text{Rh}\{\text{ArNC(NR}_2\text{NAr}\}_3]\text{PF}_6\), which were characterized by mass spectrometry and electronic absorption spectroscopy.
Furthermore, two Fe\textsuperscript{II} complexes of tetradentate tripodal ligands, [Fe(L1)(OTf)\textsubscript{2}] and [Fe(L2)(OTf)\textsubscript{2}]; where L\textsubscript{1} = N,N\text{-}bis(2-benzimidazolylmethyl)-N\text{-}(2-pyridylmethyl) amine and L\textsubscript{2} = N,N\text{-}bis[(1-methylbenzimidazol-2-yl)methyl]-N\text{-}[(pyridin-2-yl)methyl] amine; were synthesized and characterized. The $^1$H NMR spectra for [Fe(L1)(NCMe)\textsubscript{2}](OTf)\textsubscript{2} and [Fe(L2)(NCMe)\textsubscript{2}](OTf)\textsubscript{2} in CD\textsubscript{3}CN solution at ambient temperature exhibit paramagnetically shifted peaks typical of high-spin Fe\textsuperscript{II} complexes, while variable-temperature $^1$H NMR spectroscopy showed that the Fe center in [Fe(L1)(NCMe)\textsubscript{2}](OTf)\textsubscript{2} is in a spin equilibrium and that in [Fe(L2)(NCMe)\textsubscript{2}](OTf)\textsubscript{2} in the high-spin state (at 25 °C). Highly reactive oxoiron(IV) complexes were obtained by reaction of the Fe\textsuperscript{II} complexes with an excess of m-CPBA at –40 °C.

Abstract Approved: ____________________________________

Thesis Supervisor

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Title and Department

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Date
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A thesis submitted in partial fulfillment
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December 2011

Thesis Supervisor: Assistant Professor Jan-Uwe Rohde
CERTIFICATE OF APPROVAL

PH.D. THESIS

This is to certify that the Ph.D. thesis of

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has been approved by the Examining Committee for the thesis requirement for the Doctor of Philosophy degree in Chemistry at the December 2011 graduation.

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ABSTRACT

Mononuclear $[{\text{Ir}}\{\text{ArNC(NR}_2\text{)NAr}\}\{\text{C}_8\text{H}_{14}\}_2]$ complexes (where $R = \text{Me or Et}; \text{Ar} = \text{Ph or 4-MeC}_6\text{H}_4$; and $\text{C}_8\text{H}_{14} = \text{cis-cyclooctene}$) were synthesized from the neutral $N,N'$-dialkyl-$N,N''$-diarylguanidines via deprotonation and transmetalation. As confirmed by single-crystal structure determination, the guanidinato($1^-$) ligands coordinate the low-valent $d^8$ Ir$^1$ center in an $N,N'$-chelating binding mode, and the C–N distances of the CN$_3$ core suggest that these ligands function as stronger donors than related monoanionic, bidentate nitrogen-based ligands. In the reaction of the complexes with $\text{O}_2$, new $[{\text{Ir}}\{\text{ArNC(NR}_2\text{)NAr}\}_3]$ complexes were identified among the products, suggesting a new route for their synthesis.

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Similar tris(guanidinato) complexes of Rh$^{\text{III}}$, $[{\text{Rh}}\{\text{ArNC(NR}_2\text{)NAr}\}_3]$ ($R = \text{Me or Et}; \text{Ar} = \text{Ph, 4-MeC}_6\text{H}_4$ or 4-MeOC$_6\text{H}_4$), were synthesized. These complexes also were oxidized reversibly at low potentials, as compared to the corresponding tris(amidinato) and tris(triazenido) complexes. Chemical oxidation by $[\text{FeCp}_2]\text{PF}_6$ afforded thermally unstable, paramagnetic Rh$^{\text{IV}}$ compounds, $[{\text{Rh}}\{\text{ArNC(NR}_2\text{)NAr}\}_3]\text{PF}_6$, which were characterized by mass spectrometry and electronic absorption spectroscopy.
Furthermore, two Fe$^{II}$ complexes of tetradentate tripodal ligands, [Fe(L1)(OTf)$_2$] and [Fe(L2)(OTf)$_2$]; where L1 = N,N-bis(2-benzimidazolylmethyl)-N-(2-pyridylmethyl) amine and L2 = N,N-bis[(1-methylbenzimidazol-2-yl)methyl]-N-[(pyridin-2-yl)methyl] amine; were synthesized and characterized. The $^1$H NMR spectra for [Fe(L1)(NCMe)$_2$](OTf)$_2$ and [Fe(L2)(NCMe)$_2$](OTf)$_2$ in CD$_3$CN solution at ambient temperature exhibit paramagnetically shifted peaks typical of high-spin Fe$^{II}$ complexes, while variable-temperature $^1$H NMR spectroscopy showed that the Fe center in [Fe(L1)(NCMe)$_2$](OTf)$_2$ is in a spin equilibrium and that in [Fe(L2)(NCMe)$_2$](OTf)$_2$ in the high-spin state (at 25 °C). Highly reactive oxoiron(IV) complexes were obtained by reaction of the Fe$^{II}$ complexes with an excess of $m$-CPBA at −40 °C.
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CHAPTER 1
INTRODUCTION

This thesis covers the synthesis, characterization, and reactivity of iridium and rhodium complexes. The results show that \( N,N\)-dialky1-\( N',N''\)-diarylguanidinato ligands can support metal complexes in a wide range of the oxidation states (+I, +III, and +IV).

The synthesis, characterization, and application of the rare well-defined high-valent Ir and Rh complexes found in the literature will be discussed in Chapter 2. In order to stabilize electron-deficient metal centers, proper selection of a ligand system is crucial. Therefore, a series of electron-rich monoanionic nitrogen-donor ligands will be discussed in this chapter. Among these ligands, dialkylidarylguanidinato ligands, which have shown the exceptional ability to support metal center in high oxidation states, are the best candidates for approaching high-valent Ir and Rh complexes.

In Chapter 3, the preparation and characterization of Ir\(^1\) complexes bearing a dialkylidarylguanidinato and two cyclooctene ligands will be discussed. The reaction with dioxygen displayed two-phase behavior. Although the blue intermediates, which formed in the first phase, were not defined, the analysis of the green products suggested that reorganization of the complexes occurred during the reaction. If the oxidation reaction was performed in the presence of excess guanidinato ligand, well-defined tris(guanidinato) Ir\(^{III}\) complexes could be observed, providing an opportunity to explore a rational synthesis.

The synthesis and characterization of mid- to high-valent iridium and rhodium complexes will be discussed in Chapters 4 and 5. The mid-valent tris(chelate) metal complexes were prepared from the reaction of M\(^1\) (M = Ir and Rh) cyclooctene complexes, described in Chapter 3, with O\(_2\) in the presence of an excess of dialkylidarylguanidinato ligands. In order to investigate the accessibility of high-valent
metal complexes, electrochemical methods are utilized. Subsequently, the chemical oxidation with mild oxidants showed that high-valent iridium and rhodium complexes can not only be observed in voltammograms, but also can be chemically generated. The single-crystal structure determination and EPR spectroscopy indicated that the products from the oxidation of Ir$^{III}$ complexes are Ir$^{IV}$ rather than Ir$^{III}$ ligand-radical complexes. Although single crystals of the Rh$^{IV}$ complexes could not be obtained due to their thermal instability, the spectroscopic methods showed that they are analogous to their Ir$^{IV}$ counterparts and have higher redox potentials shown by the electrochemical studies.

The reactivity of the high-valent Ir$^{IV}$ and Rh$^{IV}$ complexes will be revealed in Chapter 6. The interconversion between The Ir$^{III}$ and Ir$^{IV}$ complexes is chemically reversible, and both can only be protonated at low pH (<1.4). The high-valent Ir and Rh complexes can oxidize substrates with O–H bonds. But substrates having C–H bond dissociation energies similar to those of the O–H bonds could not be oxidized.

The synthesis and characterization of two Fe$^{II}$ complexes supported by tripodal tetradentate ligands will be briefly discussed in the Appendix. The ligands were designed and synthesized in a systematic manner, and their Fe$^{II}$ complexes were characterized by UV–Vis, $^1$H NMR, VT NMR spectroscopy, and X-ray crystallography. Finally, the generation and characterization of oxoiron(IV) complexes will also be discussed here.
CHAPTER 2
BACKGROUND

2.1 Introduction

The common oxidation states of iridium and rhodium in organometallic and coordination compounds are +I and +III, whereas compounds with Ir and Rh in high oxidation states, i.e. +IV and +V, are very rare. In the case of Ir, however, some intriguing reactivity is associated with high-valent intermediates. For example, complexes of Ir$^{IV}$ and Ir$^{V}$ have been proposed as key intermediates in C–H bond activation,$^{1-4}$ oxygen atom transfer reactions,$^{5}$ and water oxidation chemistry.$^{6-10}$ Simple complexes of Ir$^{IV}$ are also known as strong one-electron oxidants.$^{11-14}$ The high reactivity and limited stability of high-valent Ir and Rh compounds often precludes their identification and characterization. One goal of the research presented herein is to gain access to more stable, well-defined complexes of Ir$^{IV}$ and Rh$^{IV}$ whose spectroscopic properties and structures can be investigated in detail. Another goal is to utilize the new complexes for a broader exploration of the chemistry of these high-valent metal centers.

The approach taken in this work involves strongly electron-releasing nitrogen-donor ligands that may stabilize metal centers in high oxidation states. Guanidinato ligands are well-known for their strongly electron-donating character in transition metal complexes but have previously not been used extensively as ligands for late transition metals. Here, tris(chelate) complexes of Ir$^{III}$ and Rh$^{III}$ with monoanionic $N,N$-dialkyl-$N',N''$-diarylguanidinato ligands have been synthesized and employed as platforms for accessing the +IV oxidation state of these metal centers. These studies have led to the
stabilization and spectroscopic and crystallographic characterization of a series of Ir$^{IV}$ and Rh$^{IV}$ complexes.

This background chapter begins with an overview of high-valent Ir intermediates involved in the activation of inert molecules and atom transfer, followed by a summary of the synthesis and characterization of known organometallic and coordination compounds of Ir$^{V}$, Ir$^{IV}$ and Rh$^{IV}$. Lastly, the electronic properties of guanidinato ligands in complexes of high-valent early transition metals are described.

2.2 High-valent Iridium and Rhodium

High-valent iridium has become an attractive target in recent years, mainly due to its role in C–H bond activation and oxygen atom transfer reactions.$^{1-5}$ The proposed mechanisms of C–H bond activation are shown in Scheme 1.$^{1}$ Two possible pathways were proposed: a) the reaction undergoes oxidative addition of R–H followed by reductive elimination of CH$_4$. The oxidation state of the Ir center changes throughout the reaction (Ir$^{III}$ $\rightarrow$ Ir$^{V}$$\rightarrow$ Ir$^{III}$ in this mechanism); b) the reaction undergoes a concerted $\sigma$-bond metathesis without change of oxidation state of the Ir center. Although the oxidative addition/reductive elimination pathway has been suggested by the theoretical studies,$^{15}$ Ir$^{V}$ species has always been proposed as the intermediates in this kind of reaction.$^{1}$

In 2000, Tilley and Bergman et. al. discovered the experimental evidence, which the Ir$^{V}$ complex was isolated, further supported an oxidative addition mechanism in C–H bond activation reactions.$^{2}$ The idea for the viability of the Ir$^{III}$ to Ir$^{V}$ C–H oxidative addition reaction was obtained by replacing the triflate (TfO$^{-}$) group with a less coordinating anion. This was accomplished by treating [Ir(C$_5$Me$_5$)(PMe$_3$)(SiPh$_2$OTf)(Ph)] with NaBAR$_f$ (BAR$_f$ = {B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$}) in an anion-exchange reaction, or
alternatively by reacting the more potent C–H bond activating complex 
[Ir(C₅Me₅)(PMe₃)(Me)(CH₂Cl₂)]BAr₆ with the tertiary silane HSiPh₃ (Scheme 2). These 
results offer the experimental support for an oxidative addition mechanism in C–H bond 
activation reactions through high-valent Ir (Scheme 1 pathway (a)).

_Scheme 1._ Possible Mechanisms of C–H Bond Activation Through High-valent Ir

Scheme adapted from _Organometallics_ 1999, 18, 2707.

_Scheme 2._ High-valent Ir in C–H Bond Activation

Further evidence for the C–H bond activation came from isolable boryl Ir$^{V}$ complexes, $[\text{Ir}(	ext{C}_5\text{Me}_5)\text{H}_2\text{X} \text{BR}_2]$, ($\text{X} = \text{H}$ or $\text{BO}_2\text{C}_2\text{Me}_4$) discovered by Hartwig $et.$ al. in 2001.\textsuperscript{3} The authors reported the generation and the isolation of a series of Ir$^{V}$ boryl polyhydrides, which react regiospecifically with alkanes to produce functionalized products. The synthesis was carried out by thermolyzing $[\text{Ir}(	ext{C}_5\text{Me}_5)\text{H}_4]$ with boranes to form boryl Ir$^{V}$ complexes, which could functionalize C–H bonds of both alkanes and benzene. For example, $1-n$-octyl-Bpin and $\text{C}_6\text{H}_5\text{Bpin}$ (Bpin = boryl pinacolate) were produced from the reaction of $[\text{Ir}(	ext{C}_5\text{Me}_5)\text{H}_3\text{BPin}]$ with octane and benzene, respectively (Scheme 3). The results demonstrate the property of the boryl group to induce C–H functionalization, and further reinforce the statement that high-valent Ir is involved in C–H bond activation.

Scheme 3. High-valent Ir in C–H Bond Activation

1-$n$-octyl-Bpin $\xrightarrow{\text{C}_8\text{H}_{18}}$ $\text{BR}_2 \equiv \text{Bpin}$ $\xrightarrow{\text{C}_6\text{H}_6}$ $\text{C}_6\text{H}_5\text{BR}_2$

BR$_2 = \text{BO}_2\text{C}_2\text{Me}_4$ (Bpin); $\text{BO}_2\text{C}_6\text{H}_4$; $\text{B(C}_6\text{H}_{11})_2$.


An interesting example of the chemical reaction through a proposed high-valent Ir intermediate was reported by Periana $et.$ al. in 2007.\textsuperscript{4} The cyclometalated Ir complex, $[\text{Ir}(\text{NN})(\text{NC})(\text{CH}_3)\text{OTf}]$ ($\text{NN} = 4,4'$-di-tert-butyl-2,2$'$-bipyridine-$\kappa^2$, $\text{NC} = 6$-phenyl-2,2$'$-bipyridine-$\kappa^2$, see Scheme 4), which reacts in a stoichiometric C–H activation reaction with benzene to generate the corresponding phenyl complex, as well as catalytic benzene C–H activation in the presence of acetic or trifluoroacetic acids. Most interestingly, this
compound also has been shown to undergo oxy-functionalization with oxidants such as PhI(OAc)$_2$ and PhI{OC(O)CF$_3$}$_2$ to generate CH$_3$X (X = AcO$^-$, CF$_3$C(O)O$^-$, TfO$^-$). The reaction could proceed via an Ir$^V$–R intermediate followed by reductive functionalization (Scheme 4). It should be noted that the high-valent Ir was proposed but not observed by authors in these reactions.

Scheme 4. High-valent Ir in C–H Bond Activation

(i) PhI(OC(O)CF$_3$)$_2$.

Scheme adapted from *Organometallics* 2007, 26, 2137.

Oxygen atom transfer reactions play important roles in biological systems$^{16,17}$ and also synthetic oxidation chemistry.$^{18}$ High-valent Ir complexes could also serve as oxygen atom transfer agents.$^5$ For example, oxotrimesityliridium(V), [IrO(mes)$_3$] (mes = 2,4,6-trimethylphenyl), could undergo degenerate oxygen atom transfer with trimesityliridium(III), [Ir(mes)$_3$] (Scheme 5). In addition, oxotrimesityliridium(V) could also undergo oxygen atom transfer to organic substrates, *i.e.* formation of triphenylphosphine oxide from the reaction of [IrO(mes)$_3$] with triphenylphosphine through oxygen atom transfer (Scheme 5).
Scheme 5. High-valent Ir in Oxygen Atom Transfer

Stable complexes of Ir$^{IV}$ have found applications as one-electron oxidants for synthetic purposes and in mechanistic studies,$^{11,12}$ whereas transient Ir$^{IV}$ species are involved in oxidatively induced C–H bond cleavage.$^{13,14}$ More recently, an Ir$^{IV}$ complex was proposed to be an intermediate in water oxidation chemistry.$^6$ A series of bis(aquo)iridium(III) complexes have been shown to robustly and efficiently catalyze the oxidation of water to dioxygen in the presence of a sacrificial oxidant, (NH$_4$)$_2$[Ce$^{IV}$(NO$_3$)$_6$] (Scheme 6), through a proposed Ir$^{IV}$ intermediate.

Scheme 6. High-valent Ir in Water Oxidation

$$2\text{H}_2\text{O} \xrightarrow{(\text{NH}_4)_2[\text{Ce}^{IV}(\text{NO}_3)_6]} \text{catalyst} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$$
Despite these developments, well-defined examples of Ir in the +IV and +V oxidation state are still limited.\textsuperscript{19,20} These include inorganic hexahalogeno complexes\textsuperscript{21,22} and several organometallic compounds\textsuperscript{5,23-27} with substituted phenyl or cyclopentadienyl ligands. The rare examples of crystallographically characterized Ir\textsuperscript{IV} complexes are shown in Scheme 7. The rarity of well-defined high-valent Ir complexes is due to their instable nature which results in difficulty in the synthesis and characterization of such complexes, especially when supported by organic ligands.

Scheme 7. Crystallographically Characterized Ir\textsuperscript{IV} Complexes

The following examples are the synthesis and characterization of existing high-valent Ir complexes. In 1965, the high-valent Ir\textsuperscript{V} compound, [Ir\textsuperscript{V}H\textsubscript{5}(PR\textsubscript{3})\textsubscript{3}], was synthesized by treatment of [Ir\textsuperscript{III}(PR\textsubscript{3})\textsubscript{3}]Cl\textsubscript{3} with LiAlH\textsubscript{4},\textsuperscript{28} although it was initially assigned as mid-valent Ir complex, [Ir\textsuperscript{III}H\textsubscript{3}(PR\textsubscript{3})\textsubscript{3}]. However, reinvestigation of the \textsuperscript{31}P and \textsuperscript{1}H NMR spectra suggests that the previous trihydrido complexes was in fact high-valent pentahydrido ones.\textsuperscript{29}
The first high-valent organoiridium(V) compound, [((C₅Me₅)IrMe₄], was prepared from the reaction of [Ir(C₅Me₅)Cl₂(μ-Cl)]₂ with Al₂Me₆ at −78 °C in the inert atmosphere following by oxidation with O₂ (from air). The product was characterized by ¹H NMR spectroscopy and mass spectrometry.²³

The extensive studies of tetrahalogenoiridium(IV) complexes were reported in 1987.³² Purple Ir⁴⁺ complexes [IrL₂Cl₄] [L = pyridine (py), PEt₃, PEr₂Ph, PErPh₂, AsEt₃, AsMe₂Ph, SME₂, or SeMe₂] were synthesized by oxidation of the Ir³⁺ anions [IrL₂Cl₄]⁻ with chlorine. Dark green [IrL₂Br₄] (L = py, PEr₂, PEr₃, AsEt₃, AsMe₂Ph, SME₂, or SME₂) were obtained similarly from [IrL₂Br₄]⁻ and Br₂. The [IrL₂Cl₄] (L = PPh₃, AsPh₃, or SbPh₃) were prepared directly from IrCl₃·ₙΗ₂O + 2L, followed by chlorination. The Ir⁴⁺ complexes have been characterized by IR, and UV–Vis spectroscopy and for the complex [Ir(AsEt₃)₂Br₄] by X-ray diffraction. The redox potentials (0.21–0.70 V vs. [FeCp₂]/[FeCp₂]⁺) were obtained by cyclic voltammetry.

Similar investigation from the same research group was explored in 1988.³³ The Ir⁴⁺ complexes cis-[Ir(L-L)Cl₄] [L-L = MeSCH₂CH₂SMe, MeSeCH₂CH₂SeMe, 2,2'-bipyridyl (bipy), or 1,10-phenanthroline (phen)] have been prepared by oxidation of the corresponding Ir³⁺ anions cis-[Ir(L-L)Cl₄]⁻ with Cl₂. These complexes were characterized by IR, UV–Vis, NMR (³¹P, ⁷⁷Se, and ¹²⁵Te) spectroscopy, and, for the complex [Ir(phen)Cl₂], by X-ray diffraction. Electrochemical studies show that [Ir(L-L)Cl₄]⁻/[Ir(L-L)Cl₄] redox couple for all complexes is nearly reversible and the redox potentials of Ir³⁺ complexes range from 0.88 to 1.22 V vs. [FeCp₂]/[FeCp₂]⁺ which are more positive than those of trans-[IrL₂Cl₄] analogues.

Neutral homoleptic organoiridium(IV) compound, [Ir(mes)₄], was synthesized from the reaction of anhydrous IrCl₃ with four-fold of mesityllithium at room temperature.²⁵ The solid-state structure showed a distorted tetrahedral geometry, and the EPR spectrum at 77 K agrees with tetrahedral low-spin d⁵ Ir complex with g∥ = 2.437 and g⊥ = 2.005. In addition, two, one-electron reversible waves were observed at −0.44 and
−1.12 V vs. [FeCp2]/[FeCp2]⁺ in cyclic voltammetry. Chemical oxidation of the this compound was carried out by using AgOTf or NOPF₆ to generate diamagnetic tetrahedral Ir⁶⁺ complexes [Ir(mes)₄]OTf or [Ir(mes)₄]PF₆ from the same research group, and [Ir(mes)₄]OTf was characterized by ¹H NMR and X-ray diffraction spectroscopy.

Another example of isolable Ir⁴⁺ complex was prepared by C–C bond cleavage of biphenylene with [Ir(cod)Cl₂]₂ (cod = 1,5-cyclooctadiene), replacement of cod by PMe₃, and insertion of the BF group on an Ir–C bond of the metallocycle (Scheme 8). It is worth noting that the complex [Ir(PMe₃)₃(biph)Cl] can be oxidized quasi-reversibly to form an Ir⁴⁺ species [Ir(PMe₃)₃(biph)Cl]⁺, which can be obtained by bulk electrolysis, but cannot be isolated as a crystalline form. Oxidation with NOBF₄ gives the unusual Ir⁴⁺ boryl compound [Ir(PMe₃)₃(biphBF)Cl]⁺, which has been isolated and structurally characterized. The EPR spectroscopic data (g = 2.15 and 1.96) confirmed that the oxidation is metal-centered.

Scheme 8. Synthesis of boryl Ir⁴⁺ complex

(i) Biphenyl, C₁₂H₁₀; (ii) 2 PMe₃; (iii) NOBF₄, NaBPh₄

For a broader exploration of the chemistry of Ir⁴⁺, however, the availability of complexes with multidentate ligands based on organic heteroatom-donor frameworks would be of great advantage, as has been the case for other high-valent transition metal centers. Although a series of stable complexes of the type [Ir⁴⁺X₄L₂]; where X = Cl,
Br and L = N-, P-, or S-donor ligand; were described two decades ago, the corresponding complexes with more than two heteroatom donors could not be obtained.\textsuperscript{32,33} Nevertheless, electrochemical studies of Ir\textsuperscript{III} complexes of phenylpyridine-derived\textsuperscript{34,35} and corrolato ligands\textsuperscript{36-38}, $E_{1/2} = 0.07$–0.91 V and 0.2 V vs. $[\text{FeCp}_2]/[\text{FeCp}_2]^+$, respectively, suggest that high-valent analogues may be within reach by proper design of coordinated ligands.

Moving up the periodic table from the third to second row, metal complexes with high oxidation state become even more difficult to achieve. Therefore, compounds containing rhodium in the +IV and +V oxidation state are more scarce. Although several organometallic rhodium(IV) compounds also have been reported,\textsuperscript{39} some of the high-valent Rh complexes are proved to be misinterpreted. For example, one class of these complexes, the mononuclear or binuclear superoxorhodium(III) ions was initially misinterpreted as Rh\textsuperscript{IV} containing compounds, Claus Blue, resulted from the oxidation of Rh\textsuperscript{III}.\textsuperscript{40} There are only a few cases of well-defined Rh\textsuperscript{IV} complexes described in the literatures (Scheme 9).\textsuperscript{41-45} Unlike octahedral $[\text{IrX}_6]^2^-$, where X = F, Br, Cl; only fluoride analogue for rhodium(IV) exists.

\textit{Scheme 9. Well-defined Rh\textsuperscript{IV} Complexes}
The diamagnetic dirhodium(IV) compound \([\{\text{Rh(Me}_3\text{CCH}_2\}]_2(\mu-\text{O})\]\) was synthesized by reaction of neopentyllithium or neopentylmagnesium bromide with \(\text{RhCl}_3(\text{THT})_3\) (THT = tetrahydrothiophen) in the presence of a source of oxygen atoms (\(\text{O}_2\) or \(\text{Me}_3\text{NO}\)).\(^4\) The \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of this compound exhibit only neopentyl resonances, and \(\nu_{\text{RhO}}\) was observed at 802 cm\(^{-1}\) in the IR spectrum. Moreover, the solid-state structure of the product was confirmed by X-ray diffraction.

The synthesis of N-confused tetraphenylporphyrin (NCTPP) rhodium(IV) complex was carried out by reaction of dirhodium(I) complex with iodine (Scheme 10).\(^4\) The product was characterized by UV–Vis, ESIMS, EPR and X-ray diffraction spectroscopy.

Therefore, as shown in the Scheme 9, nitrogen-donor-based ligands should be suitable for stabilization of \(\text{Rh}^{\text{IV}}\) complexes.

\textit{Scheme 10. Synthesis of \([\text{Rh}^{\text{IV}}(\text{NCTPP})]\text{I}_2\)}

\[
\text{NCTPP} = \text{N}-\text{confused tetraphenylporphyrin}
\]

\subsection{2.3 Mono-anionic Nitrogen Donor Ligands}

Studies involving mid- to late-transition metal complexes of nitrogen donor ligands range from classical coordination chemistry to the application fields. Among all
the types of N donor ligand systems, monoanionic nitrogen-donor ligands represent an important class of supporting ligands and have been widely used in the coordination chemistry of transition metals to impart diverse properties and reactivity. Prominent examples include poly(1-pyrazolyl)borate,\(^{46,47}\) \(\beta\)-diiminate,\(^ {48}\) aminotroponiminate,\(^ {49}\) amidinate\(^ {50,51}\) and triazenide\(^ {52}\) scaffolds (Scheme 11).

**Scheme 11. Monoanionic Nitrogen-donor Ligands**

Since guanidinates are conceptually related to the latter two systems, they may be expected to be similarly well-suited as supports for reactive metal centers. Complexes of guanidinates are known for many metals and metalloids, in particular, for early transition metals and lanthanides in mid- to high-valent oxidation states (Scheme 12).\(^ {53-59}\) For Ir and Rh, there are only a few complexes of these metal centers bearing guanidinato ligands have been reported. For example, \([\text{Ir}(H)_{2}\{\text{PhNC(NHPh)NPh}\}(\text{PPh}_3)_2]\),\(^ {60}\) \([\text{Ir}\{({}^{i}\text{Pr})\text{NC(NMe}_2\text{)N}({}^{i}\text{Pr})\}(\text{cod})]\),\(^ {61}\) \([\text{Rh}\{2,6-\text{Pr}_2\text{C}_6\text{H}_3}\text{NC(NR}_2\text{)N}(2,6-\text{Pr}_2\text{C}_6\text{H}_3)\}(\text{cod})]\),\(^ {94}\) where \(R = \text{isopropyl or cyclohexyl}\). The stabilization of high-valent metal complexes can be attributed to lone-pair donation from the nitrogen atom of the \(\text{NR}_2\) group, which increases the electron density at the two donor atoms available for metal coordination and, thereby, makes this class of ligands stronger donors than the closely related ligands (Scheme 13). Thus, in resonance form I and III, the ligand is closely related to the amidinate form bearing an amino-substituent on the central carbon atom. Amidinates are themselves an electronically flexible ligand system displaying compatibility with
transition metals in a range of oxidation states. However, the potential for a contribution from the iminium/diamide type resonance form II means that this flexibility is exceeded by guanidinates whose π-donor ability, and hence compatibility with electron-deficient metal ions, is augmented by any contribution from this resonance form. Guanidinates are therefore stronger donors (more basic) than amidinates. For a given metal, replacement of an amidinate by a guanidinate would be expected to increase the electron density on the metal and reduce its oxidation potential, e.g. [Mo\textsuperscript{II}\(_2(\mu\text{-L})_4\)] (L = PhNC(NHPh)NPh or (4-MeC\(_6\)H\(_4\))NC(H)N(4-MeC\(_6\)H\(_4\)),\textsuperscript{87,88} and, thereby, makes this class of ligands stronger donors than the closely related amidinate and triazenide anions (Scheme 14).

Scheme 12. Structures of High-Valent Metal Complexes Supported by Guanidinato Ligands

Scheme 13. Resonance Structures of the Guanidinate Monoanion

\[
\begin{align*}
&\text{I} & \quad \text{II} & \quad \text{III} \\
R'\text{N} & = & R'\text{N} & = & R'\text{N} \\
R'\text{N} & = & R'\text{N} & = & R'\text{N}
\end{align*}
\]
2.4 Conclusion

High-valent Ir and Rh complexes are capable of performing a variety of applications in chemistry. Because stable well-defined complexes of Ir and Rh in high oxidation states, e.g. +IV and +V, are very rare, systematic design and synthesis of such compounds will not only help us understand their spectroscopic and structural properties but also elucidate many reaction mechanisms, in which high-valent Ir and Rh species have been involved. The proper selection and design of supporting ligands is important to further develop this area of research. Intrigued by the reports which show the exceptional ability for stabilization of high-valent metal complexes by guanidinato ligands,\textsuperscript{53-59} we decided to take advantage of the strongly electron-releasing character of $N,N'$-dialkyl-$N'',N'''$-diarylguanidinato ligands, \{ArNC(NR\textsubscript{2})NAr\}\textsuperscript{-},\textsuperscript{64} and to investigate their potential for the stabilization of high-valent iridium and rhodium (Chapter 4, 5, and 6).
CHAPTER 3
IRIDIUM(I) COMPLEXES SUPPORTED BY \( N,N\)-DIALKYL- \( N',N''\)-DIARYLGUANIDINATO(1−) LIGANDS

3.1 Introduction

In this Chapter, the synthesis and characterization of Ir\(^{I}\) complexes of the strongly electron-donating \( N,N\)-dialkyl-\( N',N''\)-dialkyldiarylguanidinato(1−) ligands will be described. The synthesis and characterization of the ligands 1a–c and Ir\(^{I}\) complex \([\text{Ir}\{\text{PhNC(NMe}_{2}\text{)NPh}\}(\text{coe})_{2}]\) 2a (coe = cis-cyclooctene) was published by our research group in 2008.\(^{64}\) Two methods have been utilized for the synthesis of the neutral guanidines, and the corresponding lithium guanidine salts were prepared by reacting methyl lithium with free guanidines. Iridium(I) complexes supported by guanidinato ligands were synthesized by transmetallation of the lithium salts with \([\{\text{Ir(coe)}_{2}\}_{2}(\mu-\text{Cl})_{2}]\), and characterized by nuclear magnetic resonance (NMR) spectroscopy, electron impact mass spectrometry (EIMS), and elemental analysis.

As determined by spectroscopic methods and single-crystal structure determination, the guanidinato(1−) ligands coordinate the low-valent \( d^{8} \) Ir\(^{I}\) center in an \( N,N'\)-chelating binding mode. The bond lengths and angles of the intra-ligand structural features \([\text{Ir}\{\text{PhNC(NMe}_{2}\text{)NPh}\}(\text{coe})_{2}]\) show a significant contribution of the iminium/diamide resonance structure.

Complexes 2a–c are air-sensitive and react readily with dioxygen and form an unstable blue intermediate. ESI(+)MS analysis of the intermediate and final product indicates formation of dinuclear Ir complexes and a bis(guanidinato) Ir complex. In addition, for 2a, a trace amount of a tris(chelate) Ir\(^{III}\) complex was also observed by EIMS. Although these products could be observed by mass spectrometry, attempts to
isolate them were unsuccessful. However, when excess of the lithium guanidinate salt is present in solution, tris(guanidinato)iridium(III) complexes could be isolated. This result gives us valuable information for preparing and characterizing well-defined Ir$^{\text{III}}$ and Rh$^{\text{III}}$ complexes (Chapter 4, 5, and 6).

3.2 Experimental Section

**Materials and General Procedures.** All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Diethyl ether, tetrahydrofuran, and toluene were deoxygenated by sparging with N$_2$ and purified by passage through two packed columns of molecular sieves under an N$_2$ pressure (MBraun solvent purification system). $n$-Pentane was dried over Na and distilled under N$_2$ prior to use. Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using either standard Schlenk and vacuum line techniques or a glovebox. Dioxygen was dried by passage through a short column of Drierite. Isotope-enriched $^{18}$O$_2$ (97% $^{18}$O) was purchased from Cambridge Isotope Laboratories, Andover, MA, USA. [{Ir(coe)$_2$)$_2$(μ-Cl)$_2$] was synthesized according to a published procedure (coe = cis-cyclooctene). Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA.

NMR spectra were recorded on a Bruker Avance MicroBay 300 or Avance DPX 300 spectrometer at ambient temperature. $^1$H and $^{13}$C chemical shifts are reported in parts per million (ppm) and were referenced to residual solvent peaks. Mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source or on a single quadrupole ThermoFinnigan Voyager mass spectrometer using an electron impact ionization source (equipped with a solids probe). UV–Visible spectra were recorded on an HP 8453A diode array
spectrophotometer (Agilent Technologies) with samples maintained at low temperature using a cryostat from Unisoku Scientific Instruments, Japan.

\( \text{N,N'-Dimethyl-N,N''-diphenylguanidine, PhN=CNMe}_2\text{NHPh (1a).} \)

A total of 9.0 mL of a dimethylamine solution (2.0 M in THF; 18 mmol) was added to a solution of 2.01 g (8.80 mmol) of \( \text{N,N'-diphenylthiourea} \) in 15 mL of tetrahydrofuran at 0 °C. Over a period of 15 min, 2.73 g (8.77 mmol) of benzyltriethylammonium permanganate was added to the solution under stirring, resulting in the formation of a brown precipitate, and the mixture was stirred for an additional 15 min. The precipitate was separated by filtration through a celite pad and washed with tetrahydrofuran. The volatiles of the combined filtrates were removed under reduced pressure to afford a yellow oil. The guanidine was extracted from the oil with 30 mL of diethyl ether and, after evaporation of the solvent, isolated as a colorless powder. The product was recrystallized from hot hexanes and dried in vacuo. Yield: 1.49 g (71%). Anal. Calcd for \( \text{C}_{15}\text{H}_{17}\text{N}_3 \): C, 75.28; H, 7.16; N, 17.56. Found: C, 75.29; H, 7.06; N, 17.59. \( ^1\text{H} \text{NMR (300 MHz, CDCl}_3, \delta) \): 7.25 (t, \( J = 7.5 \text{ Hz} \), 4H, Ar H), 6.99 (t, \( J = 7.4 \text{ Hz} \), 2H, Ar H), 6.86 (d, \( J = 8.5 \text{ Hz} \), 4H, Ar H), 5.5 (br s, 1H, NH), 2.91 (s, 6H, NCH\(_3\)). \( ^{13}\text{C} \{^1\text{H}\} \text{ NMR (75.5 MHz, CDCl}_3, \delta) \): 151.4, 129.2, 121.9, and 120.1 (Ar), 38.1 (NCH\(_3\)). EIMS (70 eV) \( m/z \): M\(^+\) calcd for \( \text{C}_{15}\text{H}_{17}\text{N}_3 \), 239.14; found, 239.1.

\( \text{N,N'-Diethyl-N',N''-diphenylguanidine, PhN=CNEt}_2\text{NHPh (1b).} \)

A total of 1.51 mL of diethylamine (1.07 g, 14.6 mmol) was added to a solution of 1.62 g (7.10 mmol) of \( \text{N,N'-diphenylthiourea} \) in 15 mL of tetrahydrofuran at 0 °C. Over a period of 15 min, 2.23 g (7.16 mmol) of benzyltriethylammonium permanganate was added to the solution under stirring, resulting in the formation of a brown precipitate, and the mixture was stirred for an additional 15 min. The precipitate was separated by filtration through a celite pad and washed with tetrahydrofuran. The volatiles of the combined filtrates were removed under reduced pressure to afford a yellow oil. The guanidine was extracted from the oil with diethyl ether (2 x 50 mL) and, after evaporation of the solvent, isolated as a
colorless powder. The product was recrystallized from hot hexanes and dried in vacuo. Yield: 1.52 g (80%). Anal. Caled for C\textsubscript{17}H\textsubscript{21}N\textsubscript{3}: C, 76.37; H, 7.92; N, 15.72. Found: C, 76.07; H, 7.79; N, 15.66. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, \(\delta\)): 7.12 (t, \(J = 8.0\) Hz, 4H, Ar H), 6.86–6.77 (m, 6H, Ar H), 5.31 (br s, 1H, NH), 3.23 (q, \(J = 7.1\) Hz, 4H, NCH\textsubscript{2}CH\textsubscript{3}), 1.07 (t, \(J = 7.1\) Hz, 6H, NCH\textsubscript{2}CH\textsubscript{3}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (75.5 MHz, CDCl\textsubscript{3}, \(\delta\)): 150.0, 129.1, 121.8, and 118.3 (Ar), 41.9 (NCH\textsubscript{2}CH\textsubscript{3}), 12.8 (NCH\textsubscript{2}CH\textsubscript{3}). EIMS (70 eV) \textit{m}/\textit{z}: M\textsuperscript{+} calcd for C\textsubscript{17}H\textsubscript{21}N\textsubscript{3}, 267.17; found, 267.0.

\(N,N\)-Dimethyl-\(N''\),\(N''\)-bis(4-methylphenyl)guanidine, (4-MeC\textsubscript{6}H\textsubscript{4})N=C(NMe\textsubscript{2})-NH(4-MeC\textsubscript{6}H\textsubscript{4}) (1c). The procedure for the synthesis of the corresponding guanidinium iodide was adapted from a method previously described for other guanidinium iodides.\textsuperscript{68} A solution of 0.50 g (1.95 mmol) of \(N,N\)-bis(4-methylphenyl)thiourea and 1.22 mL (2.78 g, 19.5 mmol) of iodomethane in 12 mL of methanol was heated under reflux for 2 h. After the solution was cooled to room temperature, the volatiles, including unconsumed iodomethane, were removed under reduced pressure, affording \(S\)-methyl-\(N,N\)-bis(4-methylphenyl)-isothiourea hydroiodide in quantitative yield (0.78 g). To a solution of this product in 5 mL of methanol was added 1.06 mL of a dimethylamine solution (5.6 M in EtOH; 5.94 mmol). The resulting solution was heated in a sealed flask for 7 h at 70 °C. (\textit{Caution}: Due to the formation of methanethiol, which is a gas under the reaction conditions, the pressure in the flask may increase substantially. A shield should be used for protection.) The solution was then cooled to room temperature, and methanethiol was carefully removed in a stream of N\textsubscript{2}. (MeSH was trapped by routing the gas stream through concentrated HNO\textsubscript{3}.) Upon evaporation of the solvents, \(N,N\)-dimethyl-\(N''\),\(N''\)-bis(4-methylphenyl)guanidinium iodide was obtained as a colorless solid (0.73 g).

This salt was dissolved in 20 mL of diethyl ether and treated with 50 mL of a saturated aqueous Na\textsubscript{2}CO\textsubscript{3} solution. The biphasic mixture was vigorously stirred for 1 h, before the organic phase was separated and dried over MgSO\textsubscript{4} and the volatiles were removed under reduced pressure. The crude product was purified by column
chromatography on silica gel using a solution of 1% NEt₃ in diethyl ether as the eluent. Yield: 0.34 g (65%). Alternatively, the product could be recrystallized from hot hexanes and dried *in vacuo*. Anal. Calcd for C₁₇H₂₁N₃: C, 76.37; H, 7.92; N, 15.72. Found: C, 76.53; H, 8.07; N, 15.74. ¹H NMR (300 MHz, CDCl₃, δ): 7.05 (d, J = 8.4 Hz, 4H, Ar H), 6.79 (d, J = 8.4 Hz, 4H, Ar H), 5.44 (br, 1H, NH), 2.89 (s, 6H, NCH₃), 2.29 (s, 6H, C₆H₄CH₃). ¹³C{¹H} NMR (75.5 MHz, CDCl₃, δ): 152.1, 131.4, 129.9, and 120.5 (Ar), 38.2 (NCH₃), 20.8 (C₆H₄CH₃). EIMS (70 eV) m/z: M⁺ calcd for C₁₇H₂₁N₃, 267.17; found, 267.3.

**General Procedure for the Synthesis of [Ir{ArNC(NR₂)NAr}(coe)₂]**. In an N₂ atmosphere, a solution of 0.30 mmol of lithium guanidinate in 10 mL of diethyl ether was added to a suspension of 134 mg (0.150 mmol) of [{Ir(coe)₂}₂(μ-Cl)]₂ in 5 mL of diethyl ether under stirring at 20 °C. The resulting solution was stirred for 3 h, during which its color slowly turned orange and a colorless precipitate formed. After filtration of the solution, the solvent was removed under reduced pressure. The residue was recrystallized from n-pentane by preparing a concentrated solution at 20 °C and storing it at –30 °C. Orange single crystals of X-ray diffraction quality were obtained within a day.

**[Ir{PhNC(NMe₂)NPh}(coe)₂] (2a)**. Yield: 135 mg (69%). Anal. Calcd for C₃₁H₄₄IrN₃: C, 57.20; H, 6.81; N, 6.46. Found: C, 57.15; H, 6.80; N, 6.32. ¹H NMR (300 MHz, CDCl₃, δ): 7.20 (t, J = 7.8 Hz, 4H, Ar H), 6.95 (m, 6H, Ar H), 3.20 (br, 2H, =CHCH₂–), 2.57 (br, 2H, =CHCH₂–), 2.23 (s, 6H, NCH₃), 1.86–0.96 (m, 24H, =CHCH₂–). ¹³C{¹H} NMR (75.5 MHz, CDCl₃, δ): 177.9 (CN₃), 148.5, 145.3, 128.5, 128.2, 127.7, 123.8, 123.4, and 122.3 (Ar), 54.2 and 50.0 (=CHCH₂–), 39.5 (NCH₃), 30.5, 28.9, 26.3, and 26.1 (=CHCH₂–). EIMS (70 eV) m/z: M⁺ calcd for C₃₁H₄₄IrN₃, 651.32; found, 651.3. UV–Vis (toluene) λ max, nm (ε): 385 (1000), 433 (900), 480 (sh, 300).

**[Ir{PhNC(NEt₂)NPh}(coe)₂] (2b)**. Yield: 153 mg (75%). Anal. Calcd for C₃₃H₄₈IrN₃: C, 58.38; H, 7.13; N, 6.19. Found: C, 58.35; H, 7.13; N, 6.09. ¹H NMR (300 MHz, CDCl₃, δ): 7.21 (t, J = 7.8 Hz, 4H, Ar H), 6.96 (m, 6H, Ar H), 3.18 (br, 2H,
=CHCH₂–), 2.57 (m, 6H, =CHCH₂– and NCH₂CH₃), 1.86–0.96 (m, 24H, =CHCH₂–), 0.89 (t, J = 7.1 Hz, 6H, NCH₂CH₃). EIMS (70 eV) m/z: M⁺ calcd for C₃₃H₄₈IrN₃, 679.35; found, 679.5. UV–Vis (toluene) λₘₐₓ, nm (ε): 384 (1000), 430 (900), 485 (sh, 330).

[Ir{(4-MeC₆H₄)N=C(NMe₂)NH(4-MeC₆H₄)}(coe)₂] (2c). Yield: 149 mg (73%).

Anal. Calcd for C₃₃H₄₈IrN₃: C, 58.38; H, 7.13; N, 6.19. Found: C, 58.26; H, 6.97; N, 6.20. ¹H NMR (300 MHz, CDCl₃, δ): 7.03 (d, J = 8.0 Hz, 4H, Ar H), 6.90 (m, 4H, Ar H), 3.16 (br, 2H, =CHCH₂–), 2.51 (br, 2H, =CHCH₂–), 2.29 (s, 6H, NCH₃), 2.20 (s, 6H, ArCH₃), 1.90–0.80 (m, 24H, =CHC₂–). EIMS (70 eV) m/z: M⁺ calcd for C₃₃H₄₈IrN₃, 679.35; found, 679.4. UV–Vis (toluene) λₘₐₓ, nm (ε): 385 (900), 430 (800), 490 (sh, 300).

Reactions of [Ir{ArNC(NR₂)NAr}(coe)₂] Complexes with O₂. A 1.25 mM solution of the [Ir{ArNC(NR₂)NAr}(coe)₂] complex (1.25 × 10⁻³ mmol) in 1 mL of toluene was placed in a 0.5-cm UV–Vis cuvette, precooled to −40 °C and purged with O₂ (15 s). The reactions were monitored by UV–Vis spectroscopy. The solutions of an intermediate and the decay product(s) were subjected to ESI and EI mass spectrometry.

ESI(+)MS for 2a + O₂ (m/z): 240.1, 667.1, 892.8, 1131.0. For the labeling experiment, 2 mL (~44 mmol) of ¹⁸O₂ (97% ¹⁸O) was added to a solution of 1.25 × 10⁻³ mmol of 2a in 1 mL of toluene. ESI(+)MS for 2a + ¹⁸O₂ (m/z): 240.1, 667.2, 894.9, 1135.2. ESI(+)MS for 2b + O₂ (m/z): 268.2, 723.3, 949.1. ESI(+)MS for 2c + O₂ (m/z): 268.1, 723.1. For each reaction, the observed peaks can be assigned to the following ions (LH = guanidine, ArN=C(NR₂)NHAr): {LH + H}⁺, {Ir(L)₂ − 2H}⁺, {Ir₂(L)₂(O)(OH)}⁺, and {Ir₂(L)₃(O)(OH)}⁺. EIMS for 2a + O₂ (m/z): 907.4, {Ir(L)₃}⁺.

X-ray Crystallographic Analysis. A single crystal 2a was coated with Paratone N oil and mounted on a glass capillary for data collection at 150(2) K on a Nonius KappaCCD diffractometer using Mo Ka radiation (graphite monochromator). The temperature was controlled by an Oxford Cryostream Cooler (700 series, N₂ gas). Data collection, data reduction, and absorption correction were carried out following standard
CCD techniques using the software packages Collect and HKL-2000.\textsuperscript{69,70} Final cell constants were calculated from 12448 reflections from the complete data set. The space group \(P2_1/c\) was determined based on systematic absences and intensity statistics. The structure was solved by direct methods and refined by full-matrix least-squares minimization and difference Fourier methods (SHELXTL v.6.12).\textsuperscript{71,72} All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters, with the exception of the alkene hydrogen atoms (=\(\text{CH}\)), which were located in the difference Fourier map and refined with a restrained C–H distance (1.00 Å) and relative isotropic displacement parameters (1.2 times the equivalent isotropic value of the bonded carbon atom). The final full-matrix least-squares refinement converged to \(R_1 = 0.0339\) and \(wR_2 = 0.0526\) (\(F^2\), all data). Table 1 contains additional crystal and refinement information. Selected distances and angles are summarized in Tables 2 and 3.

3.3 Results and Discussion

3.3.1 Synthesis and Characterization of

\textbf{Ligands and Ir\textsuperscript{I} Complexes}

The guanidines \(\text{PhN=C(NMe}_2\text{)NHPh (1a)}\),\textsuperscript{73,74} \(\text{PhN=C(NEt}_2\text{)NHPh (1b)}\),\textsuperscript{74-76} and \((4\text{-MeC}_6\text{H}_4\text{)N=C(NMe}_2\text{)NH(4-MeC}_6\text{H}_4\text{)} (1c)\textsuperscript{73}\) were briefly mentioned in the literature but were only sparsely characterized. In this study, two different methods were utilized for the synthesis of the four neutral guanidines and complete characterization is included. The neutral ligands were synthesized from the corresponding thioureas, \(\text{ArHNC(S)NHAr}\), and the appropriate amines, \(\text{HN}_2\), according to literature methods for related compounds (Scheme 15).\textsuperscript{68,75}
Table 1. Crystallographic data and structure refinement for [Ir{PhNC(NMe2)NPh}(coe)2], 2a.

<table>
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<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{31}H_{44}IrN_{3}</td>
</tr>
<tr>
<td>Formula weight</td>
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</tr>
<tr>
<td>Crystal habit, color</td>
<td>plate, orange</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.18 x 0.17 x 0.06 mm³</td>
</tr>
<tr>
<td>Temperature, T</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength, λ</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁/c</td>
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<tr>
<td>Unit cell dimensions</td>
<td>a = 10.1479(11) Å, b = 24.521(3) Å, c = 11.5504(13) Å, β = 101.896(5)°</td>
</tr>
<tr>
<td>Volume, V</td>
<td>2812.4(6) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
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<tr>
<td>Calculated density</td>
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<td>Absorption coefficient, µ</td>
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<td>F(000)</td>
<td>1312</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>2.64 to 27.48°</td>
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<tr>
<td>Limiting indices</td>
<td>-12 ≤ h ≤ 13, -31 ≤ k ≤ 31, -14 ≤ l ≤ 14</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>22691 / 6430 [R(int) = 0.0342]</td>
</tr>
<tr>
<td>Completeness to θ</td>
<td>99.8% (θ = 27.48°)</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7628 and 0.4805</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>6429 / 0 / 334</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.071</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0240, wR2 = 0.0494</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0339, wR2 = 0.0526</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.930 and -1.367 e·Å⁻³</td>
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</table>
Table 2. Selected interatomic distances (Å) and angles (°) for [Ir{PhNC(NMe2)NPh}(coe)2], 2a.

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>Angles (°)</th>
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<tbody>
<tr>
<td>Ir–N1</td>
<td>2.122(3)</td>
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<tr>
<td>Ir–N2</td>
<td>2.118(3)</td>
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<td>Ir–C16</td>
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<tr>
<td>Ir–C17</td>
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</tr>
<tr>
<td>Ir–C24</td>
<td>2.126(3)</td>
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<tr>
<td>Ir–C25</td>
<td>2.135(3)</td>
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<tr>
<td>N1–C1</td>
<td>1.347(4)</td>
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<tr>
<td>N1–C2</td>
<td>1.427(4)</td>
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<tr>
<td>N2–C1</td>
<td>1.335(4)</td>
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<tr>
<td>N2–C8</td>
<td>1.423(4)</td>
</tr>
<tr>
<td>N3–C1</td>
<td>1.361(4)</td>
</tr>
<tr>
<td>N3–C14</td>
<td>1.457(5)</td>
</tr>
<tr>
<td>N3–C15</td>
<td>1.450(5)</td>
</tr>
<tr>
<td>C16–C17</td>
<td>1.417(5)</td>
</tr>
<tr>
<td>C24–C25</td>
<td>1.419(5)</td>
</tr>
</tbody>
</table>

C1–N1–C2 119.5(3)  
C1–N1–Ir  92.30(18)  
C2–N1–Ir  134.5(2)  
C1–N2–C8  121.4(3)  
C1–N2–Ir  92.82(19)  
C8–N2–Ir  137.8(2)  
C1–N3–C14 120.3(3)  
C1–N3–C15 123.7(3)  
C15–N3–C14 116.0(3)  
N2–C1–N1  111.7(3)  
N1–C1–N3  122.3(3)  
N2–C1–N3  126.1(3)  

* Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figure 5.
Table 3. Selected interatomic distances (Å) and angles (°) for [Ir{PhNC(NMe2)NPh}(coe)2], 2a.

<table>
<thead>
<tr>
<th>Distance / / Angle</th>
<th>Value (°/Å)</th>
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<tbody>
<tr>
<td>N1–C1–N2 / N1–Ir–N2</td>
<td>3.4(3)</td>
</tr>
<tr>
<td>N1–Ir–N2 / C16–Ir–C17</td>
<td>77.7(2)</td>
</tr>
<tr>
<td>N1–Ir–N2 / C24–Ir–C25</td>
<td>78.5(2)</td>
</tr>
<tr>
<td>C16–Ir–C17 / C24–Ir–C25</td>
<td>89.0(1)</td>
</tr>
<tr>
<td>C14–N3–C15 / N1–C1–N2</td>
<td>24.5(3)</td>
</tr>
<tr>
<td>(N1,C1,N2,N3) / (C2→C7)</td>
<td>77.8(1)</td>
</tr>
<tr>
<td>(N1,C1,N2,N3) / (C8→C13)</td>
<td>70.5(1)</td>
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</tbody>
</table>

* Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figure 1. *b* Angle between the least-squares planes of the guanidinate atoms (N1, C1, N2, and N3) and the aryl ring atoms (e.g., C2, C3, C4, C5, C6, and C7).

As for phenyl-substituted ligands 1a–b, a one-pot reaction was utilized. On the other hand, the 4-methylphenyl-substituted ligand 1c could only be prepared by the two-step route, which was proceeded by methylation of di-p-tolylthiourea with methyl iodide, amination with dimethylamine, and neutralization with sodium carbonate. As shown in Scheme 16, treatment with methyl lithium and subsequent transmetallation using [{Ir(coe)2(μ-Cl)2}] under an inert atmosphere furnished the orange IrI complexes of the anionic guanidinates, [Ir{ArNC(NR2)NAr}(coe)2], 2a–c. Complexes 2a–c are well soluble in non-polar organic solvents such as toluene, diethyl ether, and n-pentane but only sparingly soluble in acetonitrile. Unlike featureless in the UV–Vis spectra for all guanidine ligands 1a–c and their lithium guanidinate, 2a–c exhibit three distinct absorption features around 380–490 nm. The 1H NMR spectra of each of these complexes and the 13C NMR spectrum of 2a are consistent with a guanidinato-κ2N,N' and two η2-coe ligands coordinated to a d8 IrI center in a square-planar environment (Figures 1–4). The broadness of the resonance signals at 3.2 and 2.6 and in the range of 1–2 ppm may be attributed to fluxional behavior of the coe ligands in solution. On the basis of the
molecular ion peaks observed by EIMS, $2a$–$c$ were identified as mononuclear complexes. The molecular structure of $2a$ was confirmed by X-ray crystallography.

Scheme 15. Synthesis of Neutral Guanidines $1a$–$c$

$$1a, \ R = \text{Me}; \ 1b, \ R = \text{Et}$$

(i) $R_2NH$, NEt$_3$BzMnO$_4$, THF; (ii) MeI, MeOH, reflux; (iii) Me$_2$NH, MeOH, Na$_2$CO$_3$

Scheme 16. Synthesis of $[\text{Ir}\{\text{ArNC}(NR_2)N\text{Ar}\}\{\text{coe}\}_2]$ Complexes $2a$–$c$

$$a, \ R = \text{Me}, \ R' = \text{H}; \ b, \ R = \text{Et}, \ R' = \text{H}; \ c, \ R = R' = \text{Me}$$

(i) MeLi, $-40^\circ\text{C}$; (ii) 0.5 $[\text{Ir}(\text{coe})_2(\mu-\text{Cl})_2]$
Figure 1. $^1$H NMR spectrum of 2a in CDCl$_3$.

Figure 2. $^{13}$C NMR spectrum of 2a in CDCl$_3$. 
Figure 3. $^1$H NMR spectrum of $2b$ in CDCl$_3$.

Figure 4. $^1$H NMR spectrum of $2c$ in CDCl$_3$. 
3.3.2 Crystal Structure of

\([\text{Ir}\{\text{PhNC(\text{NMe}_2)\text{NPh}}\}((\text{coe})_2)]\) (2a)

Orange single crystals of 2a were grown from concentrated \(n\)-pentane solution upon standing at \(-30\) °C. The solid-state molecular structure of 2a was determined from crystallographic analysis and confirm the mononuclear nature of 2a (Figure 5 and Tables 1–3). For comparison, with amidinate ligands, both mononuclear and dinuclear complexes have been obtained.\(^{77-79}\) The Ir–N and Ir–C distances are in the ranges of 2.118(3)–2.122(3) Å and 2.126(3)–2.137(3) Å, respectively, which agree well with values of related complexes.\(^{78-81}\) Due to the acute bite angles of the chelating guanidinato ligands (N1–Ir–N2, 63.12(10)°), the metal center adopts a distorted square-planar coordination geometry. The structural analysis also reveals important intra-ligand parameters that provide insight into the bonding of the guanidinato ligands. Remarkably, the C–N distances in the planar CN\(_3\) core are nearly identical, 1.335(4)–1.361(4) Å for 2a. These parameters indicate a high degree of \(\pi\) electron delocalization over the CN\(_3\) core, implicating a significant contribution of the iminium/diamide resonance structure (Scheme 13 in Chapter 2, Structure II). In accord with the \(sp^2\) hybridization expected for efficient lone-pair donation into the CN\(_3\) unit, the N3 atom adopts a trigonal-planar geometry with bond angle sums of 360(3)°. In contrast, the N1 and N2 atoms are more pyramidalized with bond angle sums of 346.3(2)° and 352.0(2)°. Although the C14–N3–C15 and N1–C1–N2 planes are slightly twisted with respect to each other (24.5(3)°), presumably due to minor steric interactions between the NR\(_2\) alkyl and the NAr aryl groups, the conjugation of N3 and Cl \(p\) orbitals is apparently not disrupted.
The structural parameters of Ir\textsuperscript{I} complexes with the same type of guanidinato ligand but different alkenes were compared. The Ir–N and Ir–C distances for \textbf{2a} are slightly longer than those the Ir\textsuperscript{I}(cod) complexes [Ir\{PhNC(NEt\textsubscript{2})NPh\}(cod)] and [Ir\{(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})NC(NMe\textsubscript{2})N(2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\}(cod)] (cod = 1,5-cyclooctadiene, Figure 6).\textsuperscript{64} For example, the Ir–N and Ir–C distances for these two complexes are in the range of 2.069(2)–2.099(2) Å and 2.095(3)–2.122(3) Å, respectively. This could be due to the lability of the monodentate cyclooctene ligand compared to stronger binding of the bidentate 1,5-cyclooctadiene ligand. The intra-ligand parameters of \textbf{2a} and those Ir cod complexes are comparable. For instance, C–N distances in the planar CN\textsubscript{3} core of each complex are nearly identical (1.335(4)–1.361(4)). The bite angles of the chelating guanidinato ligands (N1–Ir–N2 = 63.68(9)°and 63.72(9)°), and the twist angles of C–N3–C and N1–C1–N2 (25.6(1)°and 18.7(3)° are also similar.
Figure 6. The structures of [Ir{PhNC(NEt2)NPh}(cod)] and [Ir{(2,6-Me2C6H3)NC(NMe2)N(2,6-Me2C6H3)}(cod)].

The Ir−Ccoe distances of 2a (2.126(3)–2.137(3) Å) are also comparable to other IrI(coe)2 complexes (Figure 7). For instance, the Ir−Ccoe distances for complexes [Ir(η⁶-C₆H₆)(coe)₂]PF₆, [Ir(η⁶-C₁₄H₁₀)(coe)₂]PF₆, [Ir(η⁶-C₂₀H₁₀)(coe)₂]PF₆, [Ir{S₂C(NMe₂)}(coe)₂], [Ir(N{(iPr)₂PS}₂)(coe)₂], and [Ir(N{(Ph)₂PO}₂)(coe)₂] are in the ranges of 2.128–2.173, 2.145–2.162, 2.127–2.164, 2.143–2.155, 2.148–2.163, and 2.180–2.112 Å, respectively. The cyclooctene ligands in the IrI(coe)₂ complexes including 2c exhibit a crown conformation.

Figure 7. The structures of [Ir(η⁶-C₆H₆)(coe)₂]PF₆, [Ir(η⁶-C₁₄H₁₀)(coe)₂]PF₆, [Ir(η⁶-C₂₀H₁₀)(coe)₂]PF₆, [Ir{S₂C(NMe₂)}(coe)₂], [Ir(N{(Pr)₂PS}₂)(coe)₂], and [Ir(N{(Ph)₂PO}₂)(coe)₂].
The intra-ligand structural features of 2a are unusual, because complexes of guanidinato(1–) ligands typically display more localized bonding with a longer C–N bond to the non-coordinated nitrogen atom and shorter ones to the metal-coordinated nitrogen atoms. Thus, the bonding in those guanidinate systems is best described by a relatively larger contribution of the amine/amidinate resonance structures (Scheme 13 in Chapter 2, Structure I and III). On the other hand, the greater extent of delocalization observed for 2a is present in complexes of Ti IV, Zr IV, and Nb V. It has been argued that significant involvement of the lone pair of the NR2 nitrogen atom is due to the ligands’ coordination to an electron-deficient metal center. In this context, the observations made here for low-valent d8 IrI complexes may seem surprising. Presumably, the π-acceptor alkene ligand enhances the electron-releasing character of the guanidinato ligand and thus facilitates participation of the NR2 lone pair in CN3 π bonding.

3.3.3 O2 Reactivity

In solution, complexes 2a–c react readily with dioxygen, as indicated by the disappearance of their characteristic absorption features in the UV–Vis region and appearance of a new band at ca. 660 nm (Figures 8–10). For example, at −40 °C, the formation time of a blue intermediate (λmax = 660 nm) for 2a in toluene solution with O2 is ca. 35 min (30 min, λmax = 660 nm for 2b, Figure 9; 20 min, λmax = 660 nm for 2c, Figures 10). The blue species is unstable and decays gradually to a green species (λmax = 620 nm) over time. The intermediate and final product were characterized by 1H NMR spectroscopy and mass spectrometry (Table 4). In the 1H NMR spectra, broad resonances were observed, which indicate mixture of products; possibly oligomerization of complexes could occur during oxidation. Oligomerization of complexes may be a result from dissociation of cyclooctene which was detected in the reaction of 2a with O2 by 1H NMR spectroscopy. In ESI(+)MS, one bis(guanidinato) or oxygen-containing complex
(m/z = 667, \{\text{Ir(L)}_2 - 2 \text{H}\}^+ or \{\text{2a + O}\}^+) and two dinuclear Ir complexes (m/z = 893, \{\text{Ir}_2(\text{L})_2(\text{O})(\text{OH})\}^+) and m/z = 1131, \{\text{Ir}_2(\text{L})_3(\text{O})(\text{OH})\}^+) were detected. In order to identify the species shown at m/z = 667 whether oxygen atom was involved in this ion, an isotope experiment was conducted by the reaction of 2a with \textsuperscript{18}O\textsubscript{2}. No m/z shift was observed when comparing the ESI mass spectra of 2a + \textsuperscript{16}O\textsubscript{2} to that of 2a + \textsuperscript{18}O\textsubscript{2}. Therefore, the peak shown at m/z = 667 must be due to the \{\text{Ir(L)}_2 - 2 \text{H}\}^+ ion. To confirm this assignment, 2b–c were also reacted with O\textsubscript{2}, and characterized by ESI(+)MS. Both resulted in an ion shown at m/z = 723 (\{\text{Ir(L)}_2 - 2\text{H}\}^+) in the ESI(+)MS, which is indicative of the bis(guanidinato)iridium complex. In addition, when the solution of the reaction of 2a + O\textsubscript{2} was subjected to EI mass spectrometry, one weak intensity peak shown at m/z = 907 suggested that the tris(guanidinato)iridium complex [\text{Ir}^\text{III}(\text{L})_3] was formed in this reaction. Although bis(guanidinato) and two dinuclear Ir complexes were observed in the ESI(+)MS and the trace amount of tris(guanidinato) was found in the EIMS, attempts to purify and isolate a well-defined product were unsuccessful.

\textit{Table 4.} Mass-to-charge ratios (m/z) obtained from ESI(+)MS for the reactions of 2a–c with O\textsubscript{2}. \textsuperscript{a}

<table>
<thead>
<tr>
<th>Reaction</th>
<th>m/z(calc. value)</th>
</tr>
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<tbody>
<tr>
<td>2a + O\textsubscript{2}</td>
<td>240.1(240.2), 667.1(667.2), 892.8(893.2), 1131.0(1131.3)</td>
</tr>
<tr>
<td>2a + \textsuperscript{18}O\textsubscript{2}</td>
<td>240.1(240.2), 667.2(667.2), 892.9(893.2), 1131.2(1131.3)</td>
</tr>
<tr>
<td>2a + O\textsubscript{2} (EI MS)</td>
<td>907.4(907.4)</td>
</tr>
<tr>
<td>2b + O\textsubscript{2}</td>
<td>268.2(268.2), 723.3(723.3), 949.1(949.3)</td>
</tr>
<tr>
<td>2c + O\textsubscript{2}</td>
<td>268.1(268.2), 723.1(723.3), 949.1(949.3)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}. In toluene.
The formation of bis(guanidinato) and tris(guanidinato) Ir complexes suggests reorganization of the Ir complex (dissociation of ligand from metal complex) is required to form stable products. In order to increase the yields of the bis(guanidinato) or tris(guanidinato) Ir complexes, the oxidations were carried out in the presence of excess lithium guanidinates. Although no difference in the mass spectrometry was observed when carrying out the reaction in the presence of 1 equiv of lithium guanidinate, the significant increase of intensity of the peak at \( m/z = 907 \) found in the EIMS for the reaction done in the presence of 10 equiv of lithium guanidinate suggests that the yield of tris(guanidinato) Ir complex was improved. The formation of the tris(guanidinato) Ir complex was confirmed by \(^1\)H NMR spectroscopy. This observation shows that \([\text{Ir}\{\text{ArNC}(\text{NR}_2)\text{NAr}\}(\text{coe})_2]\) complexes can serve as precursors for preparing tris(guanidinato) complexes.

Figure 8. UV–Vis spectrum of 1.25 mM 2a (orange) in toluene, the intermediate (blue) of the reaction with O\(_2\), and the decay product (green). Inset: Time course of the reaction of 2a (—, black; \( \lambda \), 660 nm). Pathlength = 0.5 cm.
Figure 9. UV–Vis spectrum of 1.25 mM 2b (orange) in toluene and the intermediate (blue) of the reaction with O₂. Inset: Time course of the reaction of 2b (—, black; λ, 660 nm). Pathlength = 0.5 cm.

Figure 10. UV–Vis spectrum of 1.25 mM 2c (orange) in toluene and the intermediate (blue) of the reaction with O₂. Inset: Time course of the reaction of 2c (—, black; λ, 660 nm). Pathlength = 0.5 cm.
3.4 Conclusion

The neutral guanidines were synthesized and used for the preparation of mononuclear [Ir(L)(coe)2] complexes via deprotonation and transmetallation under an inert atmosphere. The solid state structure of 2a shows the extent of delocalization in the CN₃ core of the guanidinato ligand. The rare complexes of a low-valent Ir center coordinated to bidentate guanidinato(1−) ligands were prepared and characterized. While the [Ir(ArNC(NR₂)NAr)(coe)₂] complexes reacted readily with O₂, investigation is needed to gain further insight into the blue intermediate. The [Ir(ArNC(NR₂)NAr)(coe)₂] complexes, containing a more labile alkene ligand, were found to be useful precursors for the synthesis of tris(guanidinato) complexes of Ir III. The latter could be isolated from the reaction with O₂ in the presence of added lithium guanidinates.
CHAPTER 4

TRIS(GUANIDINATO) COMPLEXES OF IRIDIUM(III) AND IRIDIUM(IV)

4.1 Introduction

Electron-rich tris(guanidinato) complexes of Ir\textsuperscript{III}, [Ir\{ArNC(NR\textsubscript{2})NAr\}\textsubscript{3}] (where R = Me or Et; Ar = Ph or 4-MeC\textsubscript{6}H\textsubscript{4}), were synthesized from the corresponding lithium ganidinato ligands and Ir\textsuperscript{I} precursors [Ir\{ArNC(NR\textsubscript{2})NAr\}(C\textsubscript{8}H\textsubscript{14})\textsubscript{2}] and [{Ir(coe)}\textsubscript{2}(μ-Cl)\textsubscript{2}] (C\textsubscript{8}H\textsubscript{14} = cis-cyclooctene), are air-sensitive, and can be electrochemically oxidized in two one-electron transfer steps. The first electron transfer is reversible and occurs at much lower potentials than typical for Ir\textsuperscript{III}. Chemical oxidation by [FeCp\textsubscript{2}]PF\textsubscript{6} afforded isolable, paramagnetic Ir\textsuperscript{IV} compounds, [Ir\{ArNC(NR2)NAr\}\textsubscript{3}]PF\textsubscript{6}, which were characterized by analytical and spectroscopic methods and a single-crystal structure determination, demonstrating that Ir\textsuperscript{IV} is accessible in a nitrogen-donor ligand environment. A part of the results in this Chapter has been published in 2009.\textsuperscript{99}

4.2 Experimental Section

**Materials.** All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Acetonitrile, dichloromethane, diethyl ether, tetrahydrofuran, and toluene were deoxygenated by sparging with N\textsubscript{2} and purified by passage through two packed columns of molecular sieves under an N\textsubscript{2} pressure (MBraun solvent purification system). n-Pentane was dried over Na and distilled under N\textsubscript{2} prior to use.\textsuperscript{65} Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using either standard Schlenk and vacuum
line techniques or a glovebox. Dioxygen was dried by passage through a short column of Drierite. \[ \{\text{Ir(coe)}_2\}_{2}(\mu-\text{Cl})_2 \], the guanidines PhN=C(NMe$_2$)NHPh (1a), PhN=C(NEt$_2$)NHPh (1b) and (4-MeC$_6$H$_4$)N=C(NMe$_2$)NH(4-MeC$_6$H$_4$) (1c) and the Ir$^1$
complex \([\text{Ir}\{\text{PhNC(NMe$_2$)NPh}\}(\text{coe})_2]\) (2a) (coe = cis-cyclooctene) are synthesized according to published procedures previously.$^{64,66}$ The complexes \([\text{Ir}\{\text{PhNC(NEt$_2$)NPh}\}(\text{coe})_2]\) (2b) and \([\text{Ir}\{(4-\text{MeC}_6\text{H}_4)\text{NC(NMe$_2$)N(4-MeC}_6\text{H}_4)\}}(\text{coe})_2]\) (2c) are prepared analogously to 2a. The guanidine ligand (4-MeC$_6$H$_4$)N=C(NEt$_2$)NH(4-MeC$_6$H$_4$) (1d)$^{100}$ was prepared by the same procedure as for 1c. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA.

**Physical Methods.** NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at ambient temperature. $^1$H chemical shifts are reported in parts per million (ppm) and were referenced to residual solvent peaks. Mid- and near-IR spectra were recorded on a Bruker Vertex 70 Fourier-transform IR spectrometer. Samples for the mid-IR range were prepared by grinding the solid compound with KBr and pressing the mixture into a disk. For the near-IR range, 0.1 mM solutions of the compounds in CDCl$_3$ were used. Mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source or on a double-focusing magnetic-sector Micromass, Inc., Autospec mass spectrometer using an electron impact ionization source (equipped with a solids probe). UV–Visible spectra were recorded on an HP 8454a diode array spectrophotometer (Agilent Technologies). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out with a CH Instruments potentiostat (Model 620C Electrochemical Analyzer) and a standard three-electrode configuration consisting of a Pt disc working electrode, a Pt wire counter electrode and an Ag/AgNO$_3$ reference electrode (0.01 M AgNO$_3$ in MeCN; supporting electrolyte, 0.1 M NBu$_4$ClO$_4$). The voltammograms were recorded on solutions of the analyte (0.1 mM) and the supporting electrolyte (0.1 M NBu$_4$ClO$_4$) in CH$_2$Cl$_2$ under an Ar atmosphere at 293 K (Caution: Mixtures of perchlorate salts and
metal complexes are potentially explosive and should be handled with care.) Typical measurement parameters were scan rate of 0.05 to 0.5 V·s⁻¹ for CV and a potential increment of 4 mV, an amplitude of 50 mV, and a pulse period of 0.2 s for DPV. Potentials are reported referenced to an external [FeCp₂][FeCp₂]⁺ redox system, which can be converted to the SCE scale by adding 0.48 V (SCE, aqueous saturated calomel electrode). Potentials relative to SCE can be converted to the NHE scale by adding 0.24 V (NHE, normal hydrogen electrode). Continuous-wave (CW) EPR spectra were recorded at 77 K on a Bruker EMX-61 spectrometer equipped with a liquid N₂ cold-finger Dewar flask. Typical EPR spectral parameters were an X-band microwave frequency of 9.29 GHz, a modulation frequency of 100 kHz, a modulation amplitude of 10 G, and a microwave power of 3.2 mW (sample concentration, 1 mM in CH₂Cl₂).

**General Procedure for the Synthesis of [Ir{ArNC(NR₂)NAr}₃] Complexes (Method 1).** In a typical procedure, 1.2 mmol of the N,N-dialkyl-N',N''-diarylguanidine was dissolved in 15 mL of degassed diethyl ether. The solution was cooled to –40 °C and 1.1 equiv of methyllithium (1.6 M in Et₂O) was added under stirring. The resulting solution was allowed to warm to 20 °C and stirred for 1 h. Upon removal of the volatiles under reduced pressure, the Li⁺ salt of the N,N-dialkyl-N',N''-diarylguanidinate anion, Li{ArNC(NR₂)NAr}·Et₂O, was isolated as a colorless powder and stored under rigorous exclusion of moisture. The powder could also be recrystallized from a concentrated n-pentane solution at –30 °C to afford a microcrystalline solid.

A solution of 0.30 mmol of lithium guanidinate and 0.10 mmol of [Ir{ArNC(NR₂)NAr}(coe)₂] in 10 mL of toluene was continuously purged with O₂ under stirring at 20 °C. The orange solution turned into a dark brown mixture. After 10 min, the volatiles were removed under reduced pressure. Because the [Ir{ArNC(NR₂)NAr}₃] complexes react slowly with O₂, the remaining steps were carried out in an N₂ atmosphere. The product was extracted from the residue with 30 mL of n-pentane. Upon storing this solution at 20 °C, a yellow precipitate was obtained within several days,
which was separated by filtration and washed with 5 mL of acetonitrile. The residue was recrystallized from a saturated solution in dichloromethane by slow evaporation of the solvent at 20 °C and dried \textit{in vacuo}. (It is assumed that 3a–c were obtained as racemic mixtures of \(\Delta\)-and \(\Lambda\)-enantiomers.)

\([\text{Ir}\{\text{PhNC(NMe}_2\text{)NPh}\}_3]\) (3a). Yield: 49 mg (54%). Anal. Calcd for C\(_{45}\)H\(_{48}\)IrN\(_9\): C, 59.58; H, 5.33; N, 13.90. Found: C, 59.54; H, 5.42; N, 14.04. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 6.94 (t, \(J = 7.8\) Hz, 12H, Ar H), 6.78 (t, \(J = 7.4\) Hz, 6H, Ar H), 6.62 (d, \(J = 7.8\) Hz, 12H, Ar H), 2.44 (s, 18H, NCH\(_3\)). EIMS (70 eV) \(m/z\): M\(^{+}\) calcd for C\(_{45}\)H\(_{48}\)IrN\(_9\), 907.37; found, 907.4. UV–Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\), nm (\(\varepsilon\)): 305 (60000), 362 (25000).

\([\text{Ir}\{\text{PhNC(NEt}_2\text{)NPh}\}_3]\) (3b). Yield: 41 mg (41%). Anal. Calcd for C\(_{51}\)H\(_{60}\)IrN\(_9\): C, 61.79; H, 6.10; N, 12.72. Found: C, 61.45; H, 6.04; N, 12.28. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 6.94 (t, \(J = 7.7\) Hz, 12H, Ar H), 6.81–6.72 (m, 18H, Ar H), 2.93 (m, 6H, NCH\(_2\)CH\(_3\)), 2.64 (m, 6H, NCH\(_2\)CH\(_3\)), 0.73 (t, \(J = 7.1\) Hz, 18H, NCH\(_2\)CH\(_3\)). EIMS (70 eV) \(m/z\): M\(^{+}\) calcd for C\(_{51}\)H\(_{60}\)IrN\(_9\), 991.46; found, 991.5. UV–Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\), nm (\(\varepsilon\)): 305 (60000), 363 (25000).

\([\text{Ir}\{(4-\text{MeC}_6\text{H}_4)\text{NC(NMe}_2\text{)N(4-\text{MeC}_6\text{H}_4)}\}_3]\) (3c). Yield: 43 mg (43%). Anal. Calcd for C\(_{51}\)H\(_{60}\)IrN\(_9\): C, 61.79; H, 6.10; N, 12.72. Found: C, 61.62; H, 6.19; N, 12.42. \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 6.74 (d, \(J = 8.2\) Hz, 12H, Ar H), 6.54 (d, \(J = 8.2\) Hz, 12H, Ar H), 2.41 (s, 18H, NCH\(_3\)), 2.20 (s, 18H, C\(_6\)H\(_4\)CH\(_3\)). EIMS (70 eV) \(m/z\): M\(^{+}\) calcd for C\(_{51}\)H\(_{60}\)IrN\(_9\), 991.46; found, 991.5. UV–Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\), nm (\(\varepsilon\)): 305 (49000), 365 (25000).

**General Procedure for the Synthesis of [Ir\{ArNC(NR\(_2\))NAr\}_3] Complexes (Method 2).** A solution of 0.40 mmol of lithium guanidinate and 0.05 mmol of [Ir\{ArNC(NR\(_2\))NAr\}(coe)] \(_2\) in 5 mL of toluene was stirred at 20 °C for 30 min. Subsequently, the solution mixture was purged with O\(_2\) under stirring at 20 °C for 10 min. The orange solution turned into a dark brown mixture. The volatiles were removed under reduced pressure. Because the [Ir\{ArNC(NR\(_2\))NAr\}_3] complexes react slowly with
O₂, the remaining steps were carried out in an N₂ atmosphere. The product was extracted from the residue with 30 mL of n-pentane. Upon storing this solution at 20 °C, a yellow precipitate was obtained within several days, which was separated by filtration and washed with 5 mL of acetonitrile. This product can be recrystallized from a saturated solution in dichloromethane by slow evaporation of the solvent at 20 °C, but recrystallization is not required to obtain pure product.

The yields for 2a, 2b, and 2c were 29 mg (32%), 35 mg (35%), and 34 mg (34%), respectively. The UV−Vis and ¹H NMR spectra of the products are identical to that of products synthesized by previous method.

\[ \text{[Ir\{(4-MeC₆H₄)NC(NEt₂)N(4-MeC₆H₄)}_{3}\}] \quad (3d). \]

Yield: 34 mg (32%). Anal. calcd for C₅₇H₇₂IrN₉: C, 63.66; H, 6.75; N, 11.72. Found: C, 63.25; H, 6.73; N, 11.82. ¹H NMR (300 MHz, CDCl₃, δ): 6.80 (d, J = 7.4 Hz, 12H, Ar H), 6.45 (br, 12H, Ar H), 2.96 (m, J = 6.9 Hz, 6H, NCH₂CH₃), 2.66 (m, J = 6.9 Hz, 6H, NCH₂CH₃), 2.38 (s, 18H, C₆H₄CH₃), 0.73 (t, J = 6.9 Hz, 18H, NCH₂CH₃). EIMS (70 eV) m/z: M⁺ calcd for C₅₇H₇₂IrN₉, 1075.55; found, 1075.2. UV−Vis (CH₂Cl₂) \( \lambda_{\text{max}} \), nm (ε): 307 (54000), 363 (27000).

**General Procedure for the Synthesis of [Ir{ArNC(NR₂)NAr}]₃PF₆.** In an N₂ atmosphere, a solution of 6.6 mg (0.020 mmol) of ferrocenium hexafluorophosphate in 1 mL of acetonitrile was added to a suspension of 0.020 mmol of [Ir{ArNC(NR₂)NAr}₃] 3a−d in 20 mL of dichloromethane at 20 °C. The reaction mixture immediately turned into a clear, dark violet solution, which was stirred for 1 h. The solution was concentrated to a volume of 2 mL, and 8 mL of diethyl ether was added, causing the formation of a violet precipitate. The precipitate was separated by filtration and dissolved in 10 mL of acetonitrile. This solution was filtered to remove any trace amount of unreacted [Ir{ArNC(NR₂)NAr}]₃. Upon evaporation of the solvent, the product was isolated as a solid and recrystallized by vapor diffusion of n-pentane into a dichloromethane solution at −30 °C. Dark violet to black single crystals of X-ray diffraction quality were typically
obtained within several days. (It is assumed that 4a–d were obtained as racemic mixtures of Δ- and Λ-enantiomers.)

\[\text{[Ir\{PhNC(NMe}_2\)NPh\}$_3$]PF$_6$ (4a). Yield: 19.8 mg (94%). Anal. Calcd for C$_{45}$H$_{48}$F$_6$IrN$_9$: C, 51.37; H, 4.60; N, 11.98. Found: C, 51.66; H, 4.64; N, 11.77. ESI(+)(m/z): M$^+$ calcd for C$_{45}$H$_{48}$IrN$_9$, 907.37; found, 907.2. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}$, nm (\(\varepsilon\)): 284 (64000), ~300 (sh, 59000), ~540 (2800), 696 (3100).

\[\text{[Ir\{PhNC(NEt}_2\)NPh\}$_3$]PF$_6$ (4b). Yield: 21.3 mg (94%). Anal. Calcd for C$_{51}$H$_{60}$F$_6$IrN$_9$: C, 53.91; H, 5.32; N, 11.09. Found: C, 53.73; H, 5.25; N, 10.91. ESI(+)(m/z): M$^+$ calcd for C$_{51}$H$_{60}$IrN$_9$, 991.46; found, 991.3. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}$, nm (\(\varepsilon\)): 284 (62000), 300 (59000), ~540 (2300), 692 (3000).

\[\text{[Ir\{(4-MeC}_6\text{H}_4)\text{NC(NMe}_2\)N(4-MeC}_6\text{H}_4\}$_3$]PF$_6$ (4c). Yield: 20.9 mg (92%). Anal. Calcd for C$_{51}$H$_{60}$F$_6$IrN$_9$: C, 53.91; H, 5.32; N, 11.09. Found: C, 54.14; H, 5.29; N, 11.15. ESI(+)(m/z): M$^+$ calcd for C$_{51}$H$_{60}$IrN$_9$, 991.46; found, 991.2. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}$, nm (\(\varepsilon\)): 285 (58000), ~300 (sh, 56000), ~565 (2900), 713 (3100).

\[\text{[Ir\{(4-MeC}_6\text{H}_4)\text{NC(NEt}_2\)N(4-MeC}_6\text{H}_4\}$_3$]PF$_6$ (4d). Yield: 23 mg (94%). Anal. calcd for C$_{57}$H$_{72}$F$_6$IrN$_9$: C, 56.10; H, 5.95; N, 10.33. Found: C, 56.46; H, 6.05; N, 10.09. ESI(+)(m/z): M$^+$ calcd for C$_{57}$H$_{72}$IrN$_9$, 1075.55; found, 1075.5. UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}$, nm (\(\varepsilon\)): 300 (49000), ~565 (2700), 709 (3100).

**X-ray Crystallographic Analysis.** A single crystal of 4a was coated with Paratone N oil and mounted on a glass capillary for data collection at 190(2) K on a Nonius KappaCCD diffractometer using Mo Ka radiation (graphite monochromator). The temperature was controlled by an Oxford Cryostream Cooler (700 series, N$_2$ gas). Data collection, data reduction, and absorption correction were carried out following standard CCD techniques using the software packages Collect and HKL-2000. Final cell constants were calculated from 20595 reflections from the complete data set. The chiral space group $\text{I23}$ was determined based on systematic absences and intensity statistics. The structure was solved by direct methods and refined by full-matrix least-squares
minimization and difference Fourier methods (SHELXTL v.6.12). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Inversion of the structure yielded the correct absolute structure, as indicated by the Flack x parameter and improvements in $R$ indices; the unit cell thus contains the $\Delta$-enantiomer of 4a. (Note: The largest ratio of the final least-squares parameter shift to the final standard uncertainty was larger than usual, because the Flack x parameter was negative and reset to 0 by the program.) The final full-matrix least-squares refinement $R$ indices were $R_1 = 0.0403$ and $wR_2 = 0.0674 (F^2, \text{all data})$. Table 5 contains additional crystal and refinement information. Selected distances and angles are summarized in Tables 6 and 7.
Table 5. Crystallographic data and structure refinement for [Ir{PhNC(NMe₂)NPh}₃]PF₆, 4a.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄₅H₄₈F₆IrN₉P</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1052.09</td>
</tr>
<tr>
<td>Crystal habit, color</td>
<td>prism, black</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.23 x 0.14 x 0.11 mm³</td>
</tr>
<tr>
<td>Temperature, T</td>
<td>190(2) K</td>
</tr>
<tr>
<td>Wavelength, λ</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>I23</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 20.745(3) Å</td>
</tr>
<tr>
<td>Volume, V</td>
<td>8928(2) Å</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.566 Mg·m⁻³</td>
</tr>
<tr>
<td>Absorption coefficient, ε</td>
<td>3.095 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>4216</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>3.11 to 27.86°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>–26 ≤ h ≤ 27, –27 ≤ k ≤ 27, –27 ≤ l ≤ 27</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>39519 / 3559 [R(int) = 0.0865]</td>
</tr>
<tr>
<td>Completeness to</td>
<td>99.8% (θ = 27.86°)</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7370 and 0.5299</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<td>Data / restraints / parameters</td>
<td>3559 / 0 / 208</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.126</td>
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<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R1 = 0.0312, wR2 = 0.0639</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0403, wR2 = 0.0674</td>
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<tr>
<td>Absolute structure parameter</td>
<td>0.000(8)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>1.517 and –1.056 e·Å⁻³</td>
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Table 6. Selected interatomic distances (Å) and angles (°) for [Ir{PhNC(NMe$_2$)NPh}$_3$]PF$_6$, 4a.$^a$

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir–N1</td>
<td>2.040(3)</td>
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<tr>
<td>Ir–N2</td>
<td>2.064(3)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>N1–C1</td>
<td>1.337(5)</td>
</tr>
<tr>
<td>N1–C2</td>
<td>1.409(5)</td>
</tr>
<tr>
<td>N2–C1</td>
<td>1.361(5)</td>
</tr>
<tr>
<td>N2–C8</td>
<td>1.399(5)</td>
</tr>
<tr>
<td>N3–C1</td>
<td>1.349(6)</td>
</tr>
<tr>
<td>N3–C14</td>
<td>1.458(6)</td>
</tr>
<tr>
<td>N3–C15</td>
<td>1.454(6)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>P1–F1</td>
<td>1.576(5)</td>
</tr>
<tr>
<td>P2–F2</td>
<td>1.580(4)</td>
</tr>
<tr>
<td>P2–F3</td>
<td>1.599(3)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figure 12. Symmetry operations: #1, y, z, x; #2, z, x, y; #6, –x+1, –y+2, z; #7, x, –y+2, –z+2; #8, –x+1, y, –z+2.
Table 7. Selected dihedral angles (°) for [Ir{PhNC(NMe2)NPh}3]PF6, 4a.a

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–C1–N2 / N1–Ir–N2</td>
<td>0.3(3)</td>
</tr>
<tr>
<td>C14–N3–C15 / N1–C1–N2</td>
<td>34.7(3)</td>
</tr>
<tr>
<td>(N1,C1,N2,N3) / (C2→C7)b</td>
<td>46.8(1)</td>
</tr>
<tr>
<td>(N1,C1,N2,N3) / (C8→C13)b</td>
<td>37.3(2)</td>
</tr>
</tbody>
</table>

a Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figure 12. b Angle between the least-squares planes of the guanidinate atoms (N1, C1, N2, and N3) and the aryl ring atoms (e.g., C2, C3, C4, C5, C6, and C7).

4.3 Results and Discussion

4.3.1 Synthesis of Iridium(III) Complexes

The IrIII complexes [Ir{ArNC(NR2)NAr}3]; where R = Me, Ar = Ph (3a); R = Et, Ar = Ph (3b); R = Me, Ar = 4-MeC6H4 (3c); R = Et, Ar = 4-MeC6H4 (3d); were synthesized by the reaction of the corresponding [Ir{ArNC(NR2)NAr}(coe)2] complex with the appropriate lithium guanidinate and O2.99 When 2a was reacted with O2 in the absence of lithium guanidinate in toluene solution, the color of the solution turned blue/green, and a trace amount of tris(chelate)iridium(III) complexes was observed by EIMS. Because the formation of this complex required two additional equiv of guanidinate, the reaction was carried out in the presence of an excess of lithium guanidinate in order to increase the yield of tris(chelate)iridium(III) complex. After separation of by-products, the IrIII complexes were obtained in yields of 40-50%. Upon purging with O2, the formation of precipitates, some kind of lithium salts, was observed, and the dissociation of cyclooctene was noticed and observed by 1H NMR spectroscopy. Therefore the formation of tris(guanidinato)iridium(III) complexes was potentially formed through the following steps: oxidation of O2 with Ir center to form metal-oxygen product, dissociation of cyclooctene, formation of lithium salts and tris(guanidinato)iridium(III). It is known in the literature that coordinated olefins are
prone to dissociate when Ir\(^{l}\) and Rh\(^{l}\) alkene complexes get oxidized to higher oxidation states,\(^{103}\) which weaken the affinity of olefins to Ir and Rh centers. Finally, in order to satisfy octahedron geometry, guanidinates would occupy the vacancy of the coordination site of Ir. Alternatively, 3a–d, where R = Et, Ar = 4-MeC\(_6\)H\(_4\) (3d), could also be synthesized directly from \([\{\text{Ir(coe)}\}_2(\mu-\text{Cl})_2]\), with the appropriate lithium guanidinates and dioxygen, as shown in Scheme 17. While the yields were lower than those of using \([\text{Ir}\{\text{ArNC(NR}_2\text{)NAr}\}(\text{coe})_2]\) as the starting materials, the overall yields were still comparable to the two-step method.

We also attempted to synthesize the tris(guanidinato)iridium(III) complex with a more sterically demanding ligand, \{2,6-Me\(_2\)C\(_6\)H\(_3\)NC(NMe\(_2\))N(2,6-Me\(_2\)C\(_6\)H\(_3\))\}–, but no such compounds could not be prepared by either method. Apparently, the two methyl groups in ortho position cause steric hindrance and preclude coordination of three of these ligands to the Ir center. In fact, no tris(chelate) complex of this ligand has been described. Attempted synthesis of tris(guanidinato)iridium(III) complexes from IrCl\(_3\) in ethoxyether or \([\text{Ir}\{\text{ArNC(NR}_2\text{)NAr}\}(\text{coe})_2]\) in toluene with neutral guanidines under reflux was also explored, but the yield was very insignificant (< 3%).

Scheme 17. Synthesis of Ir\(^{III}\) Compounds 3a–d.

\(\text{a, } R = \text{Me, } R' = \text{H}; \text{ b, } R = \text{Et, } R' = \text{H}; \text{ c, } R = R' = \text{Me}; \text{ Ar = 4-C}_6\text{H}_4\text{R'; d, } R = \text{Et, } R' = \text{Me}; \text{ Ar = 4-C}_6\text{H}_4\text{R';}\)

\((i) 3 \text{ equiv of Li}\{\text{ArNC(NR}_2\text{)NAr}\}, \text{ O}_2; (ii) 8 \text{ equiv of Li}\{\text{ArNC(NR}_2\text{)NAr}\}, \text{ O}_2\)
Complexes 3a–d are soluble in the chlorinated solvent CH₂Cl₂, CHCl₃, CCl₄, but the solubility is low, and they are insoluble in other common organic solvents. They were characterized by elemental analysis, EIMS, ¹H NMR and UV–Vis spectroscopy.

4.3.2 Spectroscopic Characterization of Iridium(III) Complexes

The ¹H NMR spectra of all complexes displayed a single set of resonances of ligands which indicate that the symmetric N,N’-chelating binding mode is retained in solution and the complexes are consistent with coordination to a low-spin ⁶Ir³⁺ center in the expected D₃ symmetric environment for 3a and 3c (Figures 22–25). In addition to aryl and methyl proton resonances, 3b and 3d exhibited two distinct multiplets for the protons of the diastereotopic methylene groups of the diethylamino group indicating C₃ symmetry for these two complexes in solution. The chemical shifts of the Ir³⁺ complexes are shifted upfield by (ca. 0.5 ppm for NMe₂ and ca. 0.3–0.7 ppm for NEt₂) compared to those of all groups of protons in the corresponding neutral guanidines. Unfortunately, the decent ¹³C NMR spectra could not be obtained due to the poor solubility.

4.3.3 Electrochemical Characterization of Iridium(III) Complexes

For 3a–d, the cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) all showed that these complexes can be oxidized at unusually low potentials. The CV and DPV results are in good agreement, and no reduction processes for all complexes were observed (Figure 11 for 3a, and Figures 26–28 for 3b–d).
The cyclic voltammogram of 3a, for example, displays two distinct one-electron redox events at potentials of –0.27 and 0.73 V \(E_{1/2} = (E_{pa} + E_{pc})/2\) with respect to the \([\text{FeCp}_2]/[\text{FeCp}_2]^+\) redox couple (Figure 12). The first electron transfer is a reversible, diffusion-controlled process, whose \(\Delta E_p\) values do not differ significantly for scan rates ranging from 0.05 to 0.5 V·s⁻¹ (\(\Delta E_p = E_{pa} - E_{pc}\)). Because both free guanidine, PhN=C(NMe₂)NHPh, and lithium guanidinate, Li{PhNC(NMe₂)NPh}, are irreversibly oxidized at much more positive potentials (≈ 0.66 and 0.49 V, respectively), the first redox event in 3a may be assigned to a metal-centered electron-transfer process. The second step is quasi-reversible and may be attributable to either a metal-centered or a ligand-centered process. Similar voltammograms as for 3a were obtained for 3b, 3c, and 3d, but the first redox step occurred at lower potentials, \(i.e., –0.33\) V for 3b, \(–0.41\) V for 3c, and \(–0.43\) V for 3d, in line with the increasing electron donation from the guanidinato ligand\(^\text{13}\) to the Ir center (3a < 3b < 3c < 3d).
Figure 12. Cyclic voltammograms of 0.1 mM 3a in CH$_2$Cl$_2$ (0.1 M NBu$_4$ClO$_4$) at scan rates of 0.05, 0.1, 0.2, 0.3, and 0.5 V·s$^{-1}$. Inset: Plot of anodic peak current, $i_{pa}$, versus square root of scan rate for the first ( ■, black; $R^2 = 0.9982$) and second oxidation ( ◆, red; $R^2 = 0.9861$).

By comparison, the Ir$^{III}$/Ir$^{IV}$ redox potentials of 3a–d are significantly less positive than those of many other Ir$^{III}$ complexes ($\geq 0.21$ V vs. [FeCp$_2$]/[FeCp$_2$]$^+$).$^{32,33,106}$ Even complexes with very electron-rich ligand sets such as cyclometalated tris(2-pyridylphenyl),$^{105-107}$ corrolato$^{36}$ and tris(dithiocarbamato) complexes (Figure 13),$^{108}$ which all provide a trianionic environment around the Ir center akin to the tris(guanidinato) complexes 3a–d, exhibit higher potentials (0.07–0.91 V vs. [FeCp$_2$]/[FeCp$_2$]$^+$) (Table 8).
Figure 13. Structure of Ir$^{III}$ complexes with tris(2-pyridylphenyl), tris(dithiocarbamato), and corrolato ligand environment

Table 8. Redox potential of complexes 3a–d, and cycloiridated tris(2-pyridylphenyl), corrolato and tris(dithiocarbamato) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>First redox</th>
<th>Second redox</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>−0.43</td>
<td>0.64</td>
</tr>
<tr>
<td>3c</td>
<td>−0.41</td>
<td>0.55</td>
</tr>
<tr>
<td>3b</td>
<td>−0.33</td>
<td>0.79</td>
</tr>
<tr>
<td>3a</td>
<td>−0.27</td>
<td>0.72</td>
</tr>
<tr>
<td>[Ir(R-ppy)$_3$]</td>
<td>0.07–0.91</td>
<td></td>
</tr>
<tr>
<td>[Ir(R-dtc)$_3$]</td>
<td>0.28–0.52</td>
<td></td>
</tr>
<tr>
<td>[Ir(tpfc)(NMe$_3$_2)]</td>
<td>0.20</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ vs. [FeCp$_2$]$^{0+/+}$

The effectiveness of electron-donating character from methyl substitution in para position of the benzene rings is higher than that of the extension of the alkyl substituents of the NR$_2$ group. The cyclic voltammogram shows that the second step is quasi-reversible and may be attributable to a metal-centered process (Ir$^{IV}$/Ir$^{V}$) or ligand-based
process (Ir$^{IV}$/Ir$^{V}$). If it is the Ir$^{IV}$/Ir$^{V}$ process, the second redox potentials should also follow the same trend as discussed in the first redox event (3a > 3b > 3c > 3d). However, the second redox potential follows the trend 3b > 3a > 3d > 3c which indicates the alkyl substituents in NR$_2$ groups may play less important role than substituents in para position of the aryl substituents in stabilization of Ir$^V$ complexes. However, such doubly-oxidized species cannot be concluded whether it is a metal-center ([Ir$^V$L$_3$]) or ligand-center ([Ir$^{IV}$(L)$_2$(L$^•$)])$^+$ oxidation product at this point.

If comparing the two kinds of alkyl substituents, the steric interactions between the ethyl and the aryl groups would be greater than that of methyl groups, which cause the greater twisted C–N–C and N–C–N planes in the guanidinate. Therefore, with more distorted geometry, the conjugation of the C–NEt$_2$ p orbitals would be disrupted causing a decrease in $\pi$ electron donation from the backbone nitrogen. Therefore the redox potentials for complexes bearing diethylamino groups may be higher than for complexes bearing dimethylamino group of guanidinato ligands.

### 4.3.4 Synthesis of Iridium(IV) Complexes

Chemical oxidation of 3a in dichloromethane solution with [FeCp$_2$]PF$_6$ produced [Ir{PhNC(NMe$_2$)NPh}$_3$]PF$_6$, 4a (Scheme 18), with absorption bands in the Vis–near-IR region [$\lambda_{\text{max}} = 540$ (\(\varepsilon = 2800 \text{ M}^{-1}\cdot\text{cm}^{-1}\)) and 696 nm (3100)]. Except for [FeCp$_2$]PF$_6$, another inorganic oxidizing agent, AgOTf, was also used (Scheme 18). After adding these oxidants, the color of solution changed instantaneously from pale yellow to dark purple and associated with the formation of metallic silver precipitate when using AgOTf. The Ir$^{IV}$ complexes were characterized by elemental analysis, ESI–MS, and UV–Vis spectroscopy.

In addition to inorganic oxidants, 3a ($E_{1/2} = -0.27$ V) could be oxidized by an organic oxidant, TCNE (tetracyanoethylene, $E_{1/2} = -0.27$ V), but not TCNQ (tetracyanoquinodimethane, $E_{1/2} = -0.30$ V).
The stability of 4a at 20 °C and 40 °C was examined. Only 48% decay in solution at 20 °C in four weeks suggests that the Ir IV complexes are relatively stable. It is worth noting that 4a is stable at 40 °C for ca. 1 h.

Intrigued by the formation of stable Ir IV complexes, the one pot synthesis from [{Ir(coe)2}(μ-Cl)2] or [Ir{ArNC(NR2)NAr}(coe)2] was considered and executed. Theoretically, the Ir IV complexes could be prepared by directly mixing [{Ir(coe)2}(μ-Cl)2] or [Ir{ArNC(NR2)NAr}(coe)2] and the excess of corresponding lithium guanidiantes and oxidants, [FeCp2]PF6 or AgOTf. Unfortunately, instead of formation the desired Ir IV complexes, the intractable products were observed in the mass spectroscopy.

Scheme 18. Synthesis of Ir IV Compounds 4a–d.

\[
\text{3a–d} \xrightarrow{(i)} \text{3a–d} \xrightarrow{(ii)} \text{4a–d}
\]

\(a, \text{R} = \text{Me}; \text{Ar} = \text{Ph}; b, \text{R} = \text{Et}; \text{Ar} = \text{Ph}; c, \text{R} = \text{Me}; \text{Ar} = 4\text{-MeC}_6\text{H}_4; d, \text{R} = \text{Et}; \text{Ar} = 4\text{-MeC}_6\text{H}_4\)

(i) 1 equiv of [FeCp2]PF6; (ii) 1 equiv of AgOTf

4.3.5 Spectroscopic Characterization of Iridium(IV) Complexes
As shown in Figure 14, incremental addition of [FeCp₂]PF₆ demonstrated that one equivalent is required for maximal formation of 4a, and the isosbestic point in this conversion indicates that 4a was formed directly from 3a. On a larger scale, 4a–d were generated and isolated as dark violet solids in nearly quantitative yields and analytically pure form. The complex cations, [Ir{ArNC(NR₂)NAr}₃]⁺, were identified by ESI–MS. As expected for odd-electron species, the ¹H NMR spectra of 4a–d are featureless.

![Figure 14](image)

*Figure 14. Oxidation of 0.1 mM 3a (—, black) to 4a (—, violet) in CH₂Cl₂ by addition of [FeCp₂]PF₆ in increments of 0.25 equiv as monitored by electronic absorption spectroscopy (pathlength, 0.5 cm). Inset: Corresponding changes of the absorbance at 362 (■, black) and 696 nm (◆, violet). Two little spikes at ca. 490 and 660 nm are instrumental glitches.*

The electronic spectra of the IrIII and IrIV complexes were recorded in dichloromethane solution in the range of 200–1100 nm (Figure 15). IrIII complexes 2a–d
show large transitions at 305 and 362–367 nm, which could be attributed to LMCT transition. 3a–d exhibits similar features of multiple transitions in the UV–Visible and near-IR regions: 284–285, 300–310, 540–565, 692–713, and > 1000 nm. The transitions at 284–310 having large extinction coefficients are probably due to ligand-based π-π* transitions. The transitions which displayed at the visible regions 540–565 and 692–713 nm with the extinction coefficient of about 2500–3000 cm\(^{-1}\)M\(^{-1}\) are too intense to be considered as d-d transitions. It is reasonable to assume these transitions are correlated to the electron excited from the filled ligand π orbitals to the metal d orbitals (Table 9). The near-IR spectra exhibit one band at 8700 cm\(^{-1}\) and two shoulders at 6400 and 5200 cm\(^{-1}\) (Figure 16).

![UV–Vis spectra](image)

*Figure 15. UV–Vis spectra of 0.1 mM of 4a (—, black), 4b (—, green), 4c (—, blue), and 4d (—, red) in CH\(_2\)Cl\(_2\). Pathlength = 0.5 cm.*
Table 9. Absorption maxima in the UV–Vis spectra of 3a–d and 4a–d complexes.

<table>
<thead>
<tr>
<th>Ir^III complex</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>Ir^IV complex</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>305, 362</td>
<td>4a</td>
<td>≈540, 696</td>
</tr>
<tr>
<td>3b</td>
<td>305, 363</td>
<td>4b</td>
<td>≈540, 692</td>
</tr>
<tr>
<td>3c</td>
<td>305, 365</td>
<td>4c</td>
<td>≈565, 713</td>
</tr>
<tr>
<td>3d</td>
<td>307, 367</td>
<td>4d</td>
<td>≈565, 706</td>
</tr>
</tbody>
</table>

Figure 16. Near-IR spectra of 0.1 mM 4a (—, black), 4b (—, green), 4c (—, blue), and 4d (—, red) in CDCl₃. Pathlength = 1.0 cm. The peaks in the spectra near 1900 and 2250 cm⁻¹ are due to solvent (Figure 29) absorbance in this region.

For all the Ir^IV complexes, a distinct transition in the near-IR region was observed, and the NIR spectra were investigated (As expected, Ir^III complexes do not show any feature in NIR spectra, Figure 30). As shown in Figure 16, these transitions which displayed at the regions 1150 for 4a and 4b and 1170 nm for 4c and 4d with the
extinction coefficient of about 2800–3300 cm\(^{-1}\)M\(^{-1}\) are too intense to be considered as \(d-d\) transitions. It is reasonable to assume these transitions are correlated to the charge transfer (MLCT or LMCT).

Compared to the redox potential, the trend was found that 2a–d with stronger electron-donating substituents have higher \(\lambda_{\text{max}}\) than those with weaker electron-donating substituents (2a < 2b < 2c < 2d) (Figure 17).

Moreover, the same trend (3b < 3a < 3d < 3c) was observed in Ir\(^{\text{IV}}\)/Ir\(^{\text{V}}\) oxidation potentials and the visible regions, 692–713 nm, of the 3a–d (Figure 17). Although the transition at 540 nm for 3a–b is not distinguishable (likewise, 565 nm for 3c–d), the trend, 3a–d < 3c–d, is still noticeable.

We mainly focus on the bands that are in the range of 1400–1600 cm\(^{-1}\) of IR spectra, where two of the three guanidinato \(\nu_{\text{CN}}\) are expected to be observed. These bands of 3a–d and 4a–d with their tentative assignments are given in Table 10. It was found that the complexes with the same dialkylamino substituent exhibit comparable spectra, e.g. the dimethylamino complexes 3a and 3c are similar, and the diethylamino complexes 4b and 4d are similar. They are also similar to the corresponding [Ir(L)(CO)\(_2\)] complexes
(L = guanidinato ligand). In addition to $\nu_{\text{CN}}$ of the guanidinato core, the arene CC stretching and the alkyl CH deformation vibrations could also be observed in this region. The arene CC stretching vibrations appear at $ca. 1500$ and $1570–1590 \text{ cm}^{-1}$. The alkyl CH deformation vibrations fall in the region $< 1480 \text{ cm}^{-1}$. Comparing Ir$^{\text{III}}$ complexes 3a–d to Ir$^{\text{IV}}$ complexes 4a–d, some changes were observed (Figure 18 and Figures 31–33). For instance, the group of bands at $ca. 1430 \text{ cm}^{-1}$ shifted to $ca. 1380 \text{ cm}^{-1}$, and the band shown at $ca. 1600 \text{ cm}^{-1}$ moved to $ca. 1570 \text{ cm}^{-1}$. These shifts could reflect the changes in intraligand bonding or in relative contributions of resonance structures as described in Chapter 2 (Scheme 13).

**Table 10. CN and CC stretching frequencies from IR spectra of Ir$^{\text{III}}$ and Ir$^{\text{IV}}$ complexes**

<table>
<thead>
<tr>
<th>Ir$^{\text{III}}$ complexes</th>
<th>$\nu_{\text{CN}} + \nu_{\text{CC}}$</th>
<th>$\nu_{\text{CC}}$</th>
<th>$\nu_{\text{CN}}$</th>
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<tbody>
<tr>
<td>3a</td>
<td>1594, 1575, 1553</td>
<td>1485</td>
<td>1447(sh), 1427, 1412</td>
</tr>
<tr>
<td>3b</td>
<td>1593, 1573, 1530</td>
<td>1489</td>
<td>1431, 1421</td>
</tr>
<tr>
<td>3c</td>
<td>1609, 1567, 1552</td>
<td>1504</td>
<td>1446, 1422, 1414</td>
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<tr>
<td>3d</td>
<td>1608, 1569, 1531</td>
<td>1503</td>
<td>1441, 1410(sh)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ir$^{\text{IV}}$ complexes</th>
<th>$\nu_{\text{CN}} + \nu_{\text{CC}}$</th>
<th>$\nu_{\text{CC}}$</th>
<th>$\nu_{\text{CN}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>1591, 1581, 1571</td>
<td>1484</td>
<td>1420, 1391, 1379</td>
</tr>
<tr>
<td>4b</td>
<td>1591, 1579, 1536</td>
<td>1484</td>
<td>1416, 1380</td>
</tr>
<tr>
<td>4c</td>
<td>1574, 1556</td>
<td>1503</td>
<td>1422, 1407, 1390</td>
</tr>
<tr>
<td>4d</td>
<td>1569(sh), 1535</td>
<td>1503</td>
<td>1415, 1381</td>
</tr>
</tbody>
</table>

**4.3.6 Crystal Structures of Iridium(IV) Complexes**

A crystallographic analysis on a single crystal of 4a, grown by vapor diffusion of $n$-pentane into a dichloromethane solution at $-30 \, ^\circ\text{C}$, confirmed the formation of [Ir{PhNC(NMe$_2$)NPh}$_3$]PF$_6$ (Figure 19). Crystal and structure refinement data for 4a are summarized in Table 5. Selected bond lengths and angles are given in Tables 6 and 7.
Figure 18. IR spectra of 3a and 4a in the range of 600–1650 nm.

Figure 19. Molecular structure of the complex 4a; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity; color key: pink = Ir, blue = N, gray = C, teal = P, green = F.
According to the single crystal X-ray analysis, 4a is monomeric in the solid state. The iridium center in 4a is coordinated to six nitrogen atoms of the three chelating \( \eta^2 \)-guanidinato ligands. The Ir–N distances of 2.040(3) and 2.064(3) Å agree well with those in [IrCl\(_4\)(phen)].\(^{33}\) The intra-ligand C–N and C–C distances are comparable to those of related guanidinato complexes of Ir\(^I\) and Ir\(^{III}\).\(^{60,64}\)

In contrast, the C–C distances in Ir\(^{III}\) semiquinonato and aminophenolato complexes display bond alternation, clearly indicating ligand radical character (Figure 20).\(^{109,110}\) The crystal structure thus provides evidence for the assignment of 4a as an Ir\(^{IV}\) rather than an Ir\(^{III}\)–ligand-radical species. In agreement with this assignment, the 77 K EPR spectrum of 4a in frozen solution is consistent with the presence of a low-spin \( d^5 \) Ir\(^{IV}\) center. The EPR spectrum exhibits a large \( g \) anisotropy (\( g = 2.38 \) and 1.87) and a broad line width (peak-to-peak separation \( \approx 300 \) G), indicative of localization of the unpaired electron predominantly in a metal-based orbital (Figure 21).

Figure 20. Structures of Ir\(^{III}\)–ligand-radical compounds

4.4 Conclusion

In summary, we have prepared and characterized rare examples of air-sensitive coordinatively saturated Ir\(^{III}\) complexes. Oxidation of these compounds led to the isolation of stable tris(guanidinato)iridium(IV) complexes, in which the Ir center is
exclusively coordinated by nitrogen-donor ligands. These results underscore the exceptional ability of the \(N,N\)-dialkyl-\(N''\)-diarylguanidinate anions to stabilize transition metals in high oxidation states and suggest them as excellent ancillary ligands for new high-valent Ir complexes that may be tailored to effect useful transformations.

*Figure 21.* EPR spectrum of 4a at 77 K
4.5 Supplemental Materials

Figure 22. $^1$H NMR spectrum of 3a.

Figure 23. $^1$H NMR spectrum of 3b.
Figure 24. $^1$H NMR spectrum of 3c.

Figure 25. $^1$H NMR spectrum of 3d.
Figure 26. Cyclic and DPV voltammograms of 0.1 mM $3b$ in CH$_2$Cl$_2$ (0.1 M NBu$_4$ClO$_4$) at scan rates of 0.1 V·s$^{-1}$.

Figure 27. Cyclic and DPV voltammograms of 0.1 mM $3c$ in CH$_2$Cl$_2$ (0.1 M NBu$_4$ClO$_4$) at scan rates of 0.1 V·s$^{-1}$.
Figure 28. Cyclic and DPV voltammograms of 0.1 mM 3d in CH₂Cl₂ (0.1 M NBu₄ClO₄) at scan rates of 0.1 V·s⁻¹.

Figure 29. Near-IR spectrum of CDCl₃.
Figure 30. Near-IR spectrum of 3a.

Figure 31. IR spectrum of 3b and 4b.
**Figure 32.** IR spectrum of 3c and 4c.

**Figure 33.** IR spectrum of 3d and 4d.
5.1 Introduction

Electron-rich tris(guanidinato) complexes of Rh\textsuperscript{III}, [Rh\{ArNC(NR\textsubscript{2})NAr\}\textsubscript{3}] (where R = Me or Et; Ar = Ph, 4-MeC\textsubscript{6}H\textsubscript{4} or 4-MeOC\textsubscript{6}H\textsubscript{4}), were synthesized directly from [{Rh(coe)\textsubscript{2}}\textsubscript{2}(\mu-Cl)\textsubscript{2}] and the respective lithium guanidinato precursors, are air-sensitive, and can be electrochemically oxidized in two one-electron transfer steps. The first electron transfer is reversible and occurs at much lower potentials than typical for Rh\textsuperscript{III}. The Rh\textsuperscript{III} compound [Rh\{(4-MeOC\textsubscript{6}H\textsubscript{4})NC(NMe\textsubscript{2})N(4-MeOC\textsubscript{6}H\textsubscript{4})\}\textsubscript{3}] was characterized by analytical and spectroscopic methods and a single-crystal structure determination. Chemical oxidation by ferrocinium afforded unstable, paramagnetic Rh\textsuperscript{IV} compounds, [Rh\{ArNC(NR\textsubscript{2})NAr\}\textsubscript{3}]PF\textsubscript{6}, which were characterized by analytical and spectroscopic methods.

5.2 Experimental Section

Materials. All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Acetonitrile, dichloromethane, diethyl ether, tetrahydrofuran, and toluene were deoxygenated by sparging with N\textsubscript{2} and purified by passage through two packed columns of molecular sieves under an N\textsubscript{2} pressure (MBraun solvent purification system). n-Pentane was dried over Na and distilled under N\textsubscript{2} prior to use. Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using either standard Schlenk and vacuum line techniques or a glovebox. Dioxygen was dried by passage through a short column of
Drierite. \([\{\text{Rh(coe)}_2\}_2(\mu-\text{Cl})_2]\),\(^{66,111}\) \([\text{Rh}\{\text{PhNC(Me)NPh}\}_3]\),\(^{112}\) \([\text{Rh}\{\text{PhNNNAr}\}_3]\),\(^{112}\) and \([\text{Fe}(\eta-C_5H_4\text{COMe})\text{Cp}]\text{PF}_6\)^{113} were synthesized according to a published procedure (coe = cis-cyclooctene). The \(^1\text{H}\) NMR spectra of \([\text{Rh}\{\text{PhNC(Me)NPh}\}_3]\) and \([\text{Rh}\{\text{PhNNNAr}\}_3]\) matched published ones. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA.

**Physical Methods.** NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at ambient temperature. \(^1\text{H}\) and \(^13\text{C}\) chemical shifts are reported in parts per million (ppm) and were referenced to residual solvent peaks. Mid- and near-IR spectra were recorded on a Bruker Vertex 70 Fourier-transform IR spectrometer. Samples for the mid-IR range were prepared by grinding the solid compound with KBr and pressing the mixture into a disk. For the near-IR range, 0.1 mM solutions of the compounds in CDCl\(_3\) were used. Mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source or on a double-focusing magnetic-sector Micromass, Inc., Autospec mass spectrometer using an electron impact ionization source (equipped with a solids probe). UV–Visible spectra were recorded on an HP 8453A diode array spectrophotometer (Agilent Technologies) with samples maintained at low temperature using a cryostat from Unisoku Scientific Instruments, Japan. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out with a CH Instruments potentiostat (Model 620C Electrochemical Analyzer) and a standard three-electrode configuration consisting of a Pt disc working electrode, a Pt wire counter electrode and an Ag/AgNO\(_3\) reference electrode (0.01 M AgNO\(_3\) in MeCN; supporting electrolyte, 0.1 M NBu\(_4\)ClO\(_4\)). The voltammograms were recorded on solutions of the analyte (0.1 mM) and the supporting electrolyte (0.1 M NBu\(_4\)ClO\(_4\)) in CH\(_2\)Cl\(_2\) under an Ar atmosphere at 293 K (Caution: Mixtures of perchlorate salts and metal complexes are potentially explosive and should be handled with care.) Typical measurement parameters were scan rate of 0.05 to 0.5 V·s\(^{-1}\) for CV and a potential increment of 4 mV, an amplitude of 50 mV, and a pulse...
period of 0.2 s for DPV. Potentials are reported referenced to an external
[FeCp₂]/[FeCp₂]⁺ redox system, which can be converted to the SCE scale by adding 0.48
V (SCE, aqueous saturated calomel electrode). Potentials relative to SCE can
be converted to the NHE scale by adding 0.24 V (NHE, normal hydrogen electrode).

\[ N,N'-\text{Bis}(4\text{-methoxyphenyl})\text{thiourea, } (4\text{-MeOC}_6\text{H}_4\text{NH})_2\text{C=S.} \]

The procedure for the synthesis was adapted from a method previously described for other
diarylthioureas. A solution of 2.8 mL (6.1 g, 50 mmol) of carbon disulfide, 0.44 g (13
mmol) of elemental sulfur and 6.2 g (50 mmol) of 4-methoxyaniline in 200 mL ethanol
was heated under reflux for 16 h, during which a pale purple solid was formed. After the
reaction mixture was cooled to room temperature, the solid was separated by filtration,
washed three times with 50 mL of diethyl ether and dried in vacuo. Yield: 7.1 g (49%).

\[ (4\text{-MeOC}_6\text{H}_4\text{H}_2)\text{N=C(NMe}_2\text{)NH}(4\text{-MeOC}_6\text{H}_4) \] (1e).

A solution of 2.9 g (10 mol) of \( N,N'-\text{bis}(4\text{-methoxyphenyl})\text{thiourea and 6.3 mL (14 g, 10 mmol)} \)
of iodomethane in 60 mL methanol was heated under reflux for 2 h. After the solution was cooled to room
temperature, the volatiles, including unconsumed iodomethane, were removed under
reduced pressure, affording \( S\text{-methyl}-N,N'-\text{bis}(4\text{-methoxyphenyl})\text{isothiourea hydroiodide} \)
in quantitative yield (4.2 g). To a solution of this product in 25 mL of methanol was
added 5.4 mL of a dimethylamine solution (5.6 M in EtOH; 30.5 mmol). The resulting
solution was heated in a sealed flask for 7 h at 70 °C. (Caution: Due to the formation
of methanethiol, which is a gas under the reaction conditions, the pressure in the flask may
increase substantially. A shield should be used for protection.) The solution was then
cooled to room temperature and methanethiol was carefully removed in a stream of N₂.
(MeSH was trapped by routing the gas stream through concentrated HNO₃.) Upon
evaporation of the solvents, \( N,N'-\text{dimethyl}-N',N''\text{-bis(4\text{-methoxyphenyl})guanidinium} \)
iodide was obtained as a pale yellow solid (4.1 g).

The salt was dissolved in 60 mL of diethyl ether and treated with 150 mL of a
saturated aqueous Na₂CO₃ solution. The biphasic mixture was vigorously stirred for 1 h,
before the organic phase was separated and the volatiles were removed under reduced pressure. The crude residue was then subjected to column chromatography on silica gel using a 5% NEt₃ of acetone solution as the eluent to yield the white solid 1.95 g (65%).

Anal. calcd for C₁₇H₂₁N₃O₂: C, 68.20; H, 7.07; N, 14.04. Anal. Calcd for C₁₇H₂₁N₃O₂: C, 68.20; H, 7.07; N, 14.04. Found: C, 67.73; H, 7.11; N, 13.75. ¹H NMR (300 MHz, CDCl₃, δ): 6.84–6.76 (m, 8H, Ar H), 4.82 (s, 1H, NH), 3.74 (s, 6H, C₆H₄OC₆H₃), 2.83 (s, 6H, NCH₃). ¹³C{¹H} NMR (75.5 MHz, CDCl₃, δ): 155.2, 153.0, 122.1, and 114.8 (Ar), 55.6 (C₆H₄OCH₃), 38.3 (NCH₃). EIMS (70 eV) m/z: M⁺ calcd for C₁₇H₂₁N₃O₂, 299.2; found, 299.4.

(4-MeOC₆H₄)N=C(NEt₂)NH(4-MeOC₆H₄)₂ (1f). A solution of 2.9 g (10 mol) of N,N’-bis(4-methoxyphenyl)thiourea and 6.3 mL (14 g, 10 mmol) of iodomethane in 60 mL methanol was heated under reflux for 2 h. After the solution was cooled to room temperature, the volatiles, including un consumed iodomethane, were removed under reduced pressure, affording S-methyl-N,N’-bis(4-methoxyphenyl)isothiourea hydroiodide in quantitative yield (4.2 g). To a solution of this product in 25 mL of methanol was added 1.7 mL of a dimethylamine solution (5.6 M in EtOH; 9.52 mmol). The resulting solution was heated in a sealed flask for 7 h at 70 °C. (Caution: Due to the formation of methanethiol, which is a gas under the reaction conditions, the pressure in the flask may increase substantially. A shield should be used for protection.) The solution was then cooled to room temperature and methanethiol was carefully removed in a stream of N₂. (MeSH was trapped by routing the gas stream through concentrated HNO₃.) Upon evaporation of the solvents, N,N’-dimethyl-N’,N’’-bis(4-methoxyphenyl)guanidinium iodide was obtained as a pale yellow solid (3.3 g).

The salt was dissolved in 60 mL of diethyl ether and treated with 150 mL of a saturated aqueous Na₂CO₃ solution. The biphasic mixture was vigorously stirred for 1 h, before the organic phase was separated and the volatiles were removed under reduced pressure. The crude residue was then subjected to column chromatography on silica gel
using a 5% triethylamine of acetone solution as the eluent to yield the white solid 2.2 g (67%). Anal. calcd for C_{19}H_{25}N_{3}O_{2}: C, 69.70; H, 7.70; N, 12.83.

**General Procedure for the Synthesis of \([\text{Rh}\{\text{ArNC(NR}_2)\text{NAr}\}_3]\) Complexes.** A solution of 0.40 mmol of lithium guanidinate and 0.05 mmol of \([\text{Rh}^1(\text{coe})_2(\mu-\text{Cl})_2]\) in 5 mL of toluene was stirred at 20 °C for 30 min. Subsequently, the solution mixture was purged with O_2 under stirring at 20 °C for 10 min. The orange solution turned into a dark brown mixture. The volatiles were removed under reduced pressure. Because the \([\text{Rh}\{\text{ArNC(NR}_2)\text{NAr}\}_3]\) complexes react slowly with O_2, the remaining steps were carried out in an N_2 atmosphere. The product was extracted from the residue with 30 mL of n-pentane. Upon storing this solution at 20 °C, a yellow precipitate was obtained within several days, which was separated by filtration and washed with 5 mL of acetonitrile. This product can be recrystallized from a saturated solution in dichloromethane by slow evaporation of the solvent at 20 °C, but recrystallization is not required to obtain pure product.

\([\text{Rh}\{\text{PhNC(NMe}_2)\text{NPh}\}_3]\) (5a). Yield: 29 mg (35%). Yellow microcrystallines were obtained from slow evaporation of dilute dichloromethane solution. Anal. calcd for C_{45}H_{48}N_{9}Rh: C, 66.09; H, 5.92; N, 15.41. Found: C, 65.36; H, 5.71; N, 15.20. ^1H NMR (300 MHz, CDCl_3, δ): 6.96 (t, J = 7.8 Hz, 12H, Ar H), 6.78 (t, J = 7.4 Hz, 6H, Ar H), 6.59 (d, J = 7.8 Hz, 12H, Ar H), 2.34 (s, 18H, NCH_3). EIMS (70 eV) m/z: M^+ calcd for C_{45}H_{48}N_{9}Rh, 817.31; found, 817.2. UV–Vis (CH_2Cl_2) λ_{max}, nm (ε): 221 (59000), 3273 (36000), 336 (49000).

\([\text{Rh}\{\text{PhNC(NEt}_2)\text{NPh}\}_3]\) (5b). Yield: 35 mg (39%). Yellow microcrystallines were obtained from slow evaporation of dilute dichloromethane solution. Anal. calcd for C_{51}H_{60}N_{9}Rh: C, 67.91; H, 6.70; N, 13.98. Found: C, 67.58; H, 6.31; N, 13.72. ^1H NMR (300 MHz, CDCl_3, δ): 6.96 (t, J = 7.7 Hz, 12H, Ar H), 6.79 (t, J = 7.4 Hz, 6H, Ar H), 6.70 (d, J = 7.8 Hz, 12H, Ar H), 2.88 (m, 6H, NCH_2CH_3), 2.60 (m, 6H, NCH_2CH_3), 0.68
(t, J = 7.1 Hz, 18H, NCH2CH3). EIMS (70 eV) m/z: M⁻ calcd for C51H60N9Rh, 901.40; found, 901.3. UV–Vis (CH2Cl2) λmax, nm (ε): 220 (58000), ~275 (38000), 340 (54000).

[Rh{(4-MeC6H4)NC(NMe2)N(4-MeC6H4)}3] (5c). Yield: 34 mg (38%). Yellow microcrystallines were obtained from slow evaporation of dilute dichloromethane solution. Anal. calcd for C51H60N9Rh: C, 67.91; H, 6.70; N, 13.98. Found: C, 67.51; H, 6.67; N, 13.83. ¹H NMR (300 MHz, CDCl3, δ): 6.75 (d, J = 8.4 Hz, 12H, Ar H), 6.51 (d, J = 8.2 Hz, 12H, Ar H), 2.32 (s, 18H, NCH3), 2.20 (s, 18H, ArCH3). EIMS (70 eV) m/z: M⁺ calcd for C51H60N9Rh, 901.40; found, 901.3. UV–Vis (CH2Cl2) λmax, nm (ε): 220 (53000), 275 (38000), 338 (40000).

[Rh{(4-MeC6H4)NC(NEt2)N(4-MeC6H4)}3] (5d). Yield: 34 mg (34%). Yellow microcrystallines were obtained from slow evaporation of dilute dichloromethane solution. Anal. calcd for C57H72N9Rh: C, 69.42; H, 7.36; N, 12.78. Found: C, 69.16; H, 7.36; N, 12.57. ¹H NMR (300 MHz, CDCl3, δ): 6.76 (d, J = 8.2 Hz, 12H, Ar H), 6.61 (d, J = 8.3 Hz, 12H, Ar H), 2.89 (m, 6H, NCH2CH3), 2.58 (m, 6H, NCH2CH3), 2.19 (s, 18H, ArCH3), 0.67 (t, J = 7.1 Hz, 18H, NCH2CH3). ¹³C{¹H} NMR (75 MHz, CDCl3, δ): 159.6 (CN3), 144.2, 128.6, 128.0, and 123.3 (Ar), 40.7 (NCH2CH3), 20.9 (ArCH3), 12.3 (NCH2CH3). EIMS (70 eV) m/z: M⁺ calcd for C57H72N9Rh, 985.50; found, 985.4. UV–Vis (CH2Cl2) λmax, nm (ε): 219 (53000), ~276 (35000), 342 (44000).

[Rh{(4-MeOC6H4)NC(NMe2)N(4-MeOC6H4)}3] (5e). Yield: 37 mg (37%). Yellow microcrystallines were obtained from slow evaporation of dilute dichloromethane solution. Anal. calcd for C51H60N9O6Rh: C, 61.38; H, 6.06; N, 12.63. Found: C, 62.01; H, 6.16; N, 12.92. ¹H NMR (300 MHz, CDCl3, δ): 6.56 (m, 24H, Ar H), 3.73 (s, 18H, OCH3), 2.33 (s, 18H, NCH3). ¹³C{¹H} NMR (75.5 MHz, CDCl3, δ): 161.5 (CN3), 153.3, 140.3, 124.0, and 113.0 (Ar), 55.6 (OCH3), 37.7 (NCH3). EIMS (70 eV) m/z: M⁺ calcd for C51H60N9O6Rh, 997.37; found, 997.3. UV–Vis (CH2Cl2) λmax, nm (ε): 220 (57000), ~280 (48000), ~309 (49000).
[Rh{(4-MeOC₆H₄)NC(NEt₂)N(4-MeOC₆H₄)}₃] (5f). Yield: 35 mg (32%). Yellow microcrystallines were obtained from slow evaporation of dilute dichloromethane solution. Anal. calcd for C₅₇H₇₂N₉O₆Rh: C, 63.26; H, 6.71; N, 11.65. Found: C, 64.04; H, 7.00; N, 12.05. ¹H NMR (300 MHz, CDCl₃, δ): 6.66 (d, J = 8.9 Hz, 12H, Ar H), 6.57 (d, J = 9.0 Hz, 12H, Ar H), 3.72 (s, 18 H, OCH₃), 2.89 (m, 6H, NCH₂CH₃), 2.60 (m, 6H, NCH₂CH₃), 0.67 (t, J = 7.0 Hz, 18H, NCH₂CH₃). ¹³C{¹H} NMR (75 MHz, CDCl₃, δ): 159.6 (CN₃), 153.2, 140.4, 124.0, and 113.9 (Ar), 55.5 (OCH₃), 40.7 (NCH₂CH₃), 12.7 (NCH₂CH₃). EIMS (70 eV) m/z: M⁺ calcd for C₅₇H₇₂N₉O₆Rh, 1081.47; found, 1081.4. UV–Vis (CH₂Cl₂) λmax, nm (ε): 220 (67000), ~280 (47000), ~316 (56000).

General Procedure for the Synthesis of [Rh{(4-MeOC₆H₄)NC(NR₂)N(4-MeOC₆H₄)}₃]PF₆. In an N₂ atmosphere, a solution of 6.6 mg (0.020 mmol) of ferrocenium hexafluorophosphate in 1 mL of acetonitrile was added to a solution of 0.020 mmol of [Rh{(4-OMeC₆H₄)NC(NR₂)N(4-OMeC₆H₄)}₃] in 5 mL of dichloromethane at –30 °C. The reaction mixture immediately turned into a dark green solution, which was stirred for 1 h. The solution was concentrated to a volume of 2 mL, and 8 mL of diethyl ether was added, causing the formation of a green precipitate. The precipitate was separated by filtration and dissolved in 10 mL of acetonitrile. This solution was filtered to remove any trace amount of unreacted [Rh{(4-OMeC₆H₄)NC(NMe₂)N(4-OMeC₆H₄)}₃]. Upon evaporation of the solvent, the product was isolated as a solid and recrystallized by vapor diffusion of n-pentane into a dichloromethane solution at –30 °C. Dark green to black single crystals of X-ray diffraction quality were typically obtained within several days. (It is assumed that 5a–f were obtained as racemic mixtures of Δ- and Λ-enantiomers.)

[Rh{PhNC(NMe₂)NPh}₃]PF₆ (6a). ESI(+)MS (m/z): M⁺ calcd for C₄₅H₄₈N₉Rh, 817.31; found, 817.72. UV–Vis (CH₂Cl₂) λmax, nm: 652, 927.

[Rh{PhNC(NEt₂)NPh}₃]PF₆ (6b). ESI(+)MS (m/z): M⁺ calcd for C₅₁H₆₀N₉Rh, 901.40; found, 901.17. UV–Vis (CH₂Cl₂) λmax, nm: 653, 927.
[Rh{(4-MeC₆H₄)NC(NMe₂)N(4-MeC₆H₄)}₃]PF₆ (6c). ESI(+)MS (m/z): M⁺ calcd for C₅₁H₆₀N₉Rh, 901.4; found, 901.3. UV–Vis (CH₂Cl₂) ʎₘₐₓ, nm: 677, 937.

[Rh{(4-MeC₆H₄)NC(NEt₂)N(4-MeC₆H₄)}₃]PF₆ (6d). ESI(+)MS (m/z): M⁺ calcd for C₅₇H₇₂N₉Rh, 985.50; found, 985.2. UV–Vis (CH₂Cl₂) ʎₘₐₓ, nm: 678, 935.

[Rh{(4-OMeC₆H₄)NC(NMe₂)N(4-MeOC₆H₄)}₃]PF₆ (6e). Yield: 19 mg (83%). ESI(+)MS (m/z): M⁺ calcd for C₅₁H₆₀N₉O₆Rh, 997.37; found, 997.40. UV–Vis (CH₂Cl₂) ʎₘₐₓ, nm (ε): 717 (6400), 970 (3600).

[Rh{(4-OMeC₆H₄)NC(NEt₂)N(4-MeOC₆H₄)}₃]PF₆ (6f). Yield: 22 mg (89%). ESI(+)MS (m/z): M⁺ calcd for C₅₇H₇₂N₉O₆Rh, 1081.47; found, 1081.16. UV–Vis (CH₂Cl₂) ʎₘₐₓ, nm (ε): 722 (6400), 966 (3800).

Stock solution of [Fe(η-C₅H₄COMe)Cp]PF₆. 5 mM of [Fe(η-C₅H₄COMe)Cp]PF₆ (9.3 mg, 0.025 mmol) in 5 mL MeCN was prepared. The solution must be kept under exclusion of moisture.

X-ray Crystallographic Analysis. A single crystal of 5e was coated with Paratone N oil and mounted on a glass capillary for data collection at 150(2) K on a Nonius KappaCCD diffractometer using Mo Kα radiation (graphite monochromator). The temperature was controlled by an Oxford Cryostream Cooler (700 series, N₂ gas). Data collection, data reduction, and absorption correction were carried out following standard CCD techniques using the software packages Collect and HKL-2000. Final cell constants were calculated from 12400 reflections from the complete data set. The space group P–1 was determined based on systematic absences and intensity statistics. The structure was solved by direct methods and refined by full-matrix least-squares minimization and difference Fourier methods (SHELXTL v.6.12). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full-matrix least-squares refinement R indices were R₁ = 0.0744
and $wR^2 = 0.1065$ ($F^2$, all data). Table 11 contains additional crystal and refinement information. Selected distances and angles are summarized in Tables 12 and 13.

5.3 Results and Discussion

5.3.1 Synthesis of Rhodium(III) Complexes

In this chapter, two new stronger electron-releasing guanidinato ligands, 1e and 1f, will be introduced. Since di-$(p$-methoxyphenyl)thiourea is not commercial available, it was synthesized by reaction of $p$-methoxyaniline with carbon disulfide according to a procedure from literature.\textsuperscript{114} The Rh\textsuperscript{III} complexes $[\text{Rh}\{\text{ArNC(NR}_2\text{)NAr}\}_3]$; where $R = \text{Me}, \text{Ar} = \text{Ph}$ (5a); $R = \text{Et}, \text{Ar} = \text{Ph}$ (5b); $R = \text{Me}, \text{Ar} = 4$-$\text{MeC}_6\text{H}_4$ (5c); $R = \text{Et}, \text{Ar} = 4$-$\text{MeC}_6\text{H}_4$ (5d); $R = \text{Me}, \text{Ar} = 4$-$\text{MeOC}_6\text{H}_4$ (5e); $R = \text{Et}, \text{Ar} = 4$-$\text{MeOC}_6\text{H}_4$ (5f); were synthesized by the one-pot method which involved mixing $\{\text{Rh(coe)}_2(\mu$-$\text{Cl})_2\}$ with the appropriate lithium guanidinates and dioxygen according to literature methods (Scheme 19).\textsuperscript{99} The yields were similar to those of their Ir\textsuperscript{III} counterparts. While $p$-methoxyphenyl derivatives could not be synthesized for Ir, this was successful for Rh (5e and 5f). The presence of methoxy substituents led to a dramatic improvement of the solubility in CH$_2$Cl$_2$. The Rh\textsuperscript{III} complexes were characterized by elemental analysis, EI–MS, $^1$H NMR and UV–Vis spectroscopy. The $^1$H resonance of the Rh\textsuperscript{III} complexes are shifted upfield compared to those of all groups of protons in the corresponding neutral guanidines. In addition, compared to Ir complexes, the NR$_2$ protons are more upfield shifted.
Table 11. Crystallographic data and structure refinement for [Rh\{(4-MeOC_{6}H_{4})NC(NMe_{2})N(4-MeOC_{6}H_{4})\}_{3}], 5e.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{51}H_{60}N_{9}O_{6}Rh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>997.99</td>
</tr>
<tr>
<td>Crystal habit, color</td>
<td>rod, orange yellow</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.24 x 0.09 x 0.07 mm(^3)</td>
</tr>
<tr>
<td>Temperature, (T)</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength, (\lambda)</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P-1)</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 13.6403(15) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(b = 13.8538(15) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(c = 16.2334(17) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(\alpha = 66.115(5)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(\beta = 78.793(5)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(\gamma = 60.767(5)^\circ)</td>
</tr>
<tr>
<td>Volume, (V)</td>
<td>2447.7(5) Å(^3)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.354 Mg m(^{-3})</td>
</tr>
<tr>
<td>Absorption coefficient, (\mu)</td>
<td>0.407 mm(^{-1})</td>
</tr>
<tr>
<td>(F(000))</td>
<td>1044</td>
</tr>
<tr>
<td>(\theta) range for data collection</td>
<td>2.94 to 29.07°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>(-18 \leq h \leq 18, -18 \leq k \leq 18, -22 \leq l \leq 22)</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>23366 / 13040 ([R(int) = 0.0388])</td>
</tr>
<tr>
<td>Completeness to (\theta)</td>
<td>99.6% ((\theta = 29.07^\circ))</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9720 and 0.9086</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>13040 / 80 / 690</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.032</td>
</tr>
<tr>
<td>Final (R) indices ([I&gt;2\sigma(I)])</td>
<td>(R1 = 0.0442, wR2 = 0.0950)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R1 = 0.0744, wR2 = 0.1065)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.224 and –0.742 e·Å(^{-3})</td>
</tr>
</tbody>
</table>
Table 12. Selected interatomic distances (Å) and angles (°) for [Rh{4-MeOC₆H₄}NC(NMe₂)N(4-MeOC₆H₄)}₃], 5e.

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>Angles (°)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh–N1</td>
<td>2.057(2)</td>
<td>N1–Rh–N2 64.21(8)</td>
</tr>
<tr>
<td>Rh–N2</td>
<td>2.071(2)</td>
<td>N4–Rh–N1 105.19(8)</td>
</tr>
<tr>
<td>Rh–N4</td>
<td>2.050(2)</td>
<td>N1–Rh–N5 164.58(7)</td>
</tr>
<tr>
<td>Rh–N5</td>
<td>2.062(2)</td>
<td>N1–Rh–N7 103.58(8)</td>
</tr>
<tr>
<td>Rh–N7</td>
<td>2.0629(19)</td>
<td>N1–Rh–N8 90.81(8)</td>
</tr>
<tr>
<td>Rh–N8</td>
<td>2.066(2)</td>
<td>N4–Rh–N2 91.31(8)</td>
</tr>
<tr>
<td>N1–C1</td>
<td>1.339(3)</td>
<td>N5–Rh–N2 103.56(8)</td>
</tr>
<tr>
<td>N1–C2</td>
<td>1.397(3)</td>
<td>N7–Rh–N2 164.71(8)</td>
</tr>
<tr>
<td>N2–C1</td>
<td>1.352(3)</td>
<td>N8–Rh–N2 105.56(8)</td>
</tr>
<tr>
<td>N2–C9</td>
<td>1.405(3)</td>
<td>N4–Rh–N5 64.20(8)</td>
</tr>
<tr>
<td>N3–C1</td>
<td>1.366(3)</td>
<td>N4–Rh–N7 101.19(8)</td>
</tr>
<tr>
<td>N3–C16</td>
<td>1.456(3)</td>
<td>N4–Rh–N8 160.71(8)</td>
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<td>N3–C17</td>
<td>1.450(3)</td>
<td>N5–Rh–N7 89.91(8)</td>
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<td>N4–C18</td>
<td>1.338(3)</td>
<td>N5–Rh–N8 101.98(8)</td>
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<tr>
<td>N4–C19</td>
<td>1.400(3)</td>
<td>N7–Rh–N8 63.87(8)</td>
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<td>N5–C18</td>
<td>1.347(3)</td>
<td></td>
</tr>
<tr>
<td>N5–C26</td>
<td>1.406(3)</td>
<td>C1–N1–C2 128.8(2)</td>
</tr>
<tr>
<td>N6–C18</td>
<td>1.366(3)</td>
<td>C1–N1–Rh 93.73(15)</td>
</tr>
<tr>
<td>N6–C33</td>
<td>1.451(3)</td>
<td>C2–N1–Rh 131.50(16)</td>
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<tr>
<td>N6–C34</td>
<td>1.447(3)</td>
<td>C1–N2–C9 124.4(2)</td>
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<tr>
<td>N7–C35</td>
<td>1.336(3)</td>
<td>C1–N2–Rh 92.75(14)</td>
</tr>
<tr>
<td>N7–C36</td>
<td>1.398(3)</td>
<td>C9–N2–Rh 127.79(16)</td>
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<tr>
<td>N8–C35</td>
<td>1.341(3)</td>
<td>C1–N3–C16 121.5(2)</td>
</tr>
<tr>
<td>N8–C43A</td>
<td>1.387(7)</td>
<td>C1–N3–C17 121.9(2)</td>
</tr>
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<td>N8–C43B</td>
<td>1.451(11)</td>
<td>C17–N3–C16 115.9(2)</td>
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<td>N9–C35</td>
<td>1.372(3)</td>
<td>N1–C1–N2 109.2(2)</td>
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<tr>
<td>N9–C50</td>
<td>1.445(3)</td>
<td>N1–C1–N3 125.2(2)</td>
</tr>
<tr>
<td>N9–C51</td>
<td>1.444(4)</td>
<td>N2–C1–N3 125.6(2)</td>
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</table>

* Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figure 14.
Table 13. Selected dihedral angles (°) for \([\text{Rh}\{(4-\text{MeOC}_6\text{H}_4)\text{NC}(\text{NMe}_2)\text{N}(4-\text{MeOC}_6\text{H}_4)\}_3\}], 5e.\(^a\)

| Dihedral Angle | \(\pm\) Uncertainty
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–C1–N2 / N1–Ir–N2</td>
<td>3.3(5)</td>
</tr>
<tr>
<td>C14–N3–C15 / N1–C1–N2</td>
<td>30.0(5)</td>
</tr>
<tr>
<td>(N1,C1,N2,N3) / (C2→C7)(^b)</td>
<td>41.5(1)</td>
</tr>
<tr>
<td>(N1,C1,N2,N3) / (C9→C14)(^b)</td>
<td>51.9(1)</td>
</tr>
<tr>
<td>N4–C18–N5 / N4–Rh–N5</td>
<td>6.3(2)</td>
</tr>
<tr>
<td>C33–N6–C34 / N4–C18–N5</td>
<td>32.8(2)</td>
</tr>
<tr>
<td>(N4,C18,N5,N6) / (C19→C24)(^b)</td>
<td>39.3(1)</td>
</tr>
<tr>
<td>(N4,C18,N5,N6) / (C26→C31)(^b)</td>
<td>48.7(1)</td>
</tr>
<tr>
<td>N7–C35–N8 / N7–Rh–N8</td>
<td>0.2(2)</td>
</tr>
<tr>
<td>C50–N9–C51 / N7–C35–N8</td>
<td>37.2(2)</td>
</tr>
<tr>
<td>(N7,C35,N8,N9) / (C36→C41)(^b)</td>
<td>37.1(1)</td>
</tr>
<tr>
<td>(N7,C35,N8,N9) / (C43A→C48A)(^b)</td>
<td>39.3(2)</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figure 14. \(^b\) Angle between the least-squares planes of the guanidinate atoms (e.g., N1, C1, N2, and N3) and the aryl ring atoms (e.g., C2, C3, C4, C5, C6, and C7).

Scheme 19. Synthesis of Rh\(^{III}\) Compounds 5a–f

\(\text{Scheme 19. Synthesis of Rh}^{\text{III}} \text{ Compounds 5a–f}\)

\[\begin{align*}
a, R = \text{Me}, \text{Ar} = \text{Ph}; & \quad b, R = \text{Et}, \text{Ar} = \text{Ph}; \\
c, R = \text{Me}; & \quad \text{Ar} = 4-\text{C}_6\text{H}_4\text{Me}; \\
d, R = \text{Et}, \text{Ar} = 4-\text{C}_6\text{H}_4\text{Me}; & \quad e, R = \text{Me}; \\
f, R = \text{Et}, \text{Ar} = 4-\text{C}_6\text{H}_4\text{OMe}; & \quad (i) 8 \text{ equiv of Li}\{\text{ArNC(NR}_2)\text{NAr}\}, \text{O}_2
\end{align*}\]
5.3.2 Spectroscopic Characterization of Rhodium(III) Complexes

Complexes 5a–d only sparsely dissolve in chlorinated solvents such as CH₂Cl₂, CHCl₃, and are insoluble in other common organic solvents, while complexes 5e–f are very soluble in CH₂Cl₂. They were characterized by elemental analysis, EI–MS, ¹H NMR and UV–Vis spectroscopy. As was the case for Ir³⁺, the ¹H NMR spectra of the Rh³⁺ complexes displayed a single set of resonances, indicating that the symmetric N,N’-chelating binding mode is retained in solution and consistent with coordination to a low-spin d⁶ Rh³⁺ center in the expected D₃ symmetric environment (Figures 37–42). Compounds 5a–f were isolated as racemic mixtures (Δ- and Λ-enantiomers), and their molecular composition was established by analytical and spectroscopic methods. In addition to aryl and methyl proton resonances, 3b and 3d exhibited two distinct multiplets for the protons of the diastereotopic methylene groups of the diethylamino group indicating C₃ symmetry for these two complexes in solution. The resonances of Rh³⁺ complexes are shifted upfield compared to in the corresponding neutral guanidines. Owing to the methoxy group, the solubility for 5e and 5f increases dramatically so that ¹³C NMR can be obtained for these two compounds.

5.3.3 Crystal Structures of Rhodium(III) Complexes

A crystallographic analysis on a single crystal of 5e, grown by vapor diffusion of n-pentane into a dichloromethane solution at –30 °C, confirmed the formation of [Rh{(4-MeC₆H₄)NC(NMe₂)N(4-MeC₆H₄)}₃] (Figure 22). Crystal and structure refinement data for 5e are summarized in Table 11. Selected bond lengths and angles are given in Tables 12 and 13.

According to the single crystal X-ray analysis, 5e is monomeric in the solid state. The rhodium center in 5e is coordinated to six nitrogen atoms of the three chelating κ²-
guanidinato ligands. The Rh–N distances of 2.065(2) and 2.057(2) Å agree well with those in [Rh{PhNNNPh}$_3$] and [Rh{PhNC(Me)NPh}$_3$]. The intra-ligand C–N and C–C distances are comparable to those of related guanidinato complexes of Rh$^{1,60}$. Due to the acute bite angle of the chelating guanidinato ligand (N–Rh–N, 63.89(8)–64.21(8)$^\circ$), the metal center adopts a distorted octahedron coordination geometry. The structural analysis also reveals important intra-ligand parameters that provide insight into the bonding of the guanidinato ligands. The C–N distances in the planar CN$_3$ core of 5e are nearly identical, 1.336(3)–1.372(3) Å. These parameters indicate a high degree of $\pi$ electron delocalization over the CN$_3$ core, implicating a significant contribution of the iminium/diamide resonance structure (Scheme 13 in Chapter 2, Structure II). In accord with the $sp^2$ hybridization expected for efficient lone-pair donation into the CN$_3$ unit, the N3 (or N6, N9) atom adopts a trigonal-planar geometry with bond angle sums of 360(2)$^\circ$. In contrast, the N1 (or N4, N7) and N2 (or N5, N8) atoms are more pyramidalized with bond angle sums of 344.9(2)–355.2(2)$^\circ$.

The intra-ligand structural features of 5e are unusual, because complexes of guanidinato(1–) ligands typically display more localized bonding with a longer C–N bond to the non-coordinated nitrogen atom and shorter ones to the metal-coordinated nitrogen atoms$^{60,85-94}$ Thus, the bonding in those guanidinate systems is best described by a relatively larger contribution of the amine/amidinate resonance structures (Scheme 13 in Chapter 2, Structure I and III). On the other hand, the greater extent of delocalization observed for 2a is also present in complexes of Ti$^{IV}$, Zr$^{IV}$, and Nb$^{V}$.$^{98}$
5.3.4 Electrochemical Characterization of Rhodium(III) Complexes

For Rh\textsuperscript{III} complexes, 5a–f, the cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) all showed that these complexes can be oxidized at unusually low potentials. The CV and DPV results are in good agreement, and no reduction processes for any complexes were observed (Figures 43–48). Electrochemical measurements for 5a–d exhibited two one-electron oxidation processes, and three one-electron oxidation processes were found for 5e–f. Previous studies on the Ir\textsuperscript{III} complexes have shown that the first redox event is reversible and the second event is quasi-reversible process. For 5a, the reversibility of the first redox event varies with scan...
window (Figure 23). For the full scan window (−2 to 2 V), two redox events were exhibited, where the first one is quasi-reversible and the second one is irreversible. However, when the scan window was narrowed down to the first redox region (−0.3 to 0.4 V), reversibility was observed. This could result from the EC mechanism. Moreover, the trends of the first redox potentials follow the electron-donating strength from the guanidinato ligand to the metal centers.

Figure 35. Cyclic voltammograms of 0.1 mM 5a in CH₂Cl₂ (0.1 M NBu₄ClO₄) at scan rates of 0.1 V·s⁻¹ from −2 to 2 V. Inset: Scan window from −0.3 to 0.4 V.

Compared to Ir³⁺ counterparts, the first redox process of 5a–d exhibited at higher potential (Table 14). Interestingly, if compared the electron-donating strength of both methyl and methoxy substituents in para position of the benzene rings and the extension of the alkyl substituents of the NR₂ group, the former has much stronger influences in terms of redox potentials than the latter. Whether the second redox events are metal or ligand based is not known at this time. The voltammograms of complexes 5e and 5f show three redox steps, and the irreversible electron transfer is attributable to a ligand-centered
process.

Table 14. $E_{1/2}$ of 0.1 mM M(III) Guanidinato Complexes in CH$_2$Cl$_2$ at a Scan Rate at 0.1 V/s.$^a$

<table>
<thead>
<tr>
<th></th>
<th>Ir$^{IV}$ Redox potential (V)</th>
<th>Rh$^{IV}$ Redox potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>$-0.27$</td>
<td>$0.09$</td>
</tr>
<tr>
<td>4b</td>
<td>$-0.33$</td>
<td>$0.06$</td>
</tr>
<tr>
<td>4c</td>
<td>$-0.41$</td>
<td>$-0.05$</td>
</tr>
<tr>
<td>4d</td>
<td>$-0.43$</td>
<td>$-0.06$</td>
</tr>
<tr>
<td>6a</td>
<td>$0.09$</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>$0.06$</td>
<td></td>
</tr>
<tr>
<td>6c</td>
<td>$-0.05$</td>
<td></td>
</tr>
<tr>
<td>6d</td>
<td>$-0.06$</td>
<td></td>
</tr>
<tr>
<td>6e</td>
<td></td>
<td>$-0.12$</td>
</tr>
<tr>
<td>6f</td>
<td></td>
<td>$-0.13$</td>
</tr>
</tbody>
</table>

$^a$ vs. [FeCp$_2$]/[FeCp$_2$]$^+$

By comparison, the Rh$^{III}$/Rh$^{IV}$ redox potentials of 5a–f are significantly less positive than those of many other Rh$^{III}$ complexes (Table 15) ($\geq 0.53$ V vs. [FeCp$_2$]/[FeCp$_2$]$^+$). Compared to the oxidation potential of this series of Rh$^{III}$ analogues, replacement of an amidinate by a guanidinate would be expected to increase the electron density on the metal and reduce its oxidation potential, and, thereby, makes this class of ligands stronger donors than the closely related amidinate and triazenide anions. In addition to oxidation potential, the voltammogram of 5a analogues, [Rh{PhNC(Me)NPh}$_3$] and [Rh(PhNNNPh)$_3$], exhibit irreversibility.

Table 15. $E_{pa}$ of 0.1 mM 5a, [Rh{PhNC(Me)NPh}$_3$], and [Rh(PhNNNPh)$_3$] in CH$_2$Cl$_2$ at a Scan Rate at 0.1 V/s.$^a$

<table>
<thead>
<tr>
<th></th>
<th>5a</th>
<th>[Rh{PhNC(Me)NPh}$_3$]</th>
<th>[Rh(PhNNNPh)$_3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.13</td>
<td>0.53</td>
</tr>
</tbody>
</table>

$^a$ vs. [FeCp$_2$]/[FeCp$_2$]$^+$
Similar to Ir$^{III}$ counterparts, the oxidation of 5a–f was studied by using ferrocenium derivatives or AgOTf. Chemical oxidation of 5e in dichloromethane solution with [FeCp$_2$]PF$_6$ produced [Rh{(4-MeOC$_6$H$_4$)NC(NMe$_2$)N(4-MeOC$_6$H$_4$)}$_3$]PF$_6$, 6e (Scheme 20), with absorption bands in the Vis–near-IR region [$\lambda_{\text{max}} = 714$ (\(\epsilon = 5200\) M$^{-1}$·cm$^{-1}$) and 983 nm (2600)]. After adding these oxidants, the color of solution changed instantaneously from pale yellow to yellow green and associated with the formation of metallic silver precipitate when using AgOTf. However, depending on different Rh$^{III}$ complexes, the choice of ferrocenium derivatives varies, i.e. [FeCp$_2$]PF$_6$ can be used to generate 6e–f from 5e–f, but for 5a–d, only [FeCp(\(\eta^5\)-C$_5$H$_4$COCH$_3$)]PF$_6$ is strong enough to oxidize Rh$^{III}$ to Rh$^{IV}$. The Rh$^{IV}$ complexes were characterized by ESI–MS and UV–Vis spectroscopy. Because of the instability of the Rh$^{IV}$ complexes, elemental analysis could not be obtained.

Scheme 20. Synthesis of Rh$^{IV}$ Compounds 6a–f.

\[\begin{align*}
6a &- f \quad \text{(i)} \\
5a &- f \quad \text{(ii)}
\end{align*}\]

\(a, R = \text{Me}; \ Ar = \text{Ph}; \ b, R = \text{Et}; \ Ar = \text{Ph}; \ c, R = \text{Me}; \ Ar = 4-\text{MeC}_6\text{H}_4; \ d, R = \text{Et}; \ Ar = 4-\text{MeC}_6\text{H}_4; \ e, R = \text{Me}; \ Ar = 4-\text{MeOC}_6\text{H}_4; \ f, R = \text{Et}; \ Ar = 4-\text{MeOC}_6\text{H}_4\)

\(\text{(i)}\) 1 equiv of [FeCp$_2$]PF$_6$ or [FeCp(\(\eta^5\)-C$_5$H$_4$COCH$_3$)]PF$_6$, \(\text{(ii)}\) 1 equiv of AgOTf
Rh\textsuperscript{IV} complexes 6a–f were unstable, and their $t_{1/2}$ values were evaluated using UV–Vis spectroscopy at ambient temperature (Figure 49 and Table 16). As can be seen, the compounds with ethyl substituents are more stable than others with methyl substituents. Although the stability trend (6f > 6d > 6b > 6e > 6c > 6a) does not follow the redox potential (6f > 6e > 6d > 6c > 6b > 6a), the correlation between electron donating strength of guanidinato ligands and the stability of Rh\textsuperscript{IV} complexes can still be observed, e.g. all ethyl substituent complexes are more stable than all methyl ones. The possible explanation for the greater stability of the complexes with ethyl substituents could be that the metal center is better protected than that in methyl substituents.

Table 16. Redox potential (V) and Stability ($t_{1/2}$) of 6a–f at 20 °C.

<table>
<thead>
<tr>
<th>Rh\textsuperscript{IV}</th>
<th>Redox potential (V)</th>
<th>$t_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>0.09</td>
<td>15</td>
</tr>
<tr>
<td>6b</td>
<td>0.06</td>
<td>28</td>
</tr>
<tr>
<td>6c</td>
<td>−0.05</td>
<td>20</td>
</tr>
<tr>
<td>6d</td>
<td>−0.06</td>
<td>73</td>
</tr>
<tr>
<td>6e</td>
<td>−0.12</td>
<td>23</td>
</tr>
<tr>
<td>6f</td>
<td>−0.13</td>
<td>102</td>
</tr>
</tbody>
</table>

5.3.6 Spectroscopic Characterization

Rhodium(IV) Complexes

As shown in Figure 24, incremental addition of [FeCp\textsubscript{2}]PF\textsubscript{6} demonstrated that one equivalent is required for maximal formation of 6e, and the isosbestic point in this conversion indicates that 6e was formed directly from 5e. The complex cations, [Rh\{ArNC(NR\textsubscript{2})NAr\}\textsubscript{3}]\textsuperscript{+}, were identified by ESI(+)–MS.

The electronic spectra of 6a–f were recorded in dichloromethane solution in the range 200–1100 nm (Figure 49). 6a–f exhibits similar features of multiple transitions in
the UV–Visible and near-IR regions: < 300, 652–722, 927–970 nm (Table 17). High extinction coefficients for the intense transitions < 300 nm indicate that these are most likely ligand-based $\pi$-$\pi^*$ transitions. The bands in the visible region 652–722 nm with extinction coefficients of about 2400–6400 cm$^{-1}$M$^{-1}$ are too intense to be considered as $d$-$d$ transitions. It is reasonable to assume these transitions are correlated to the electron excited from the filled ligand $\pi$ orbitals to the vacancy in the metal $t_{2g}$ subshell. Likewise, the bands in the region of 927–970 nm with extinction coefficients of about 1800–3800 cm$^{-1}$M$^{-1}$ are also considered as the electron excited from the filled ligand $\pi$ orbitals to the vacancy in the metal $t_{2g}$ subshell.

Figure 36. Oxidation of 0.1 mM 5e (—, yellow) to 6e (—, green) in CH$_2$Cl$_2$ by addition of [FeCp$_2$]PF$_6$ in increments of 0.25 equiv as monitored by electronic absorption spectroscopy (pathlength, 0.5 cm). Inset: Corresponding changes of the absorbance at 717 nm (◆, green).
Table 17. Absorption maxima in the UV–Vis-NIR spectra of 5a–f and 6a–f complexes.

<table>
<thead>
<tr>
<th>Rh&lt;sup&gt;III&lt;/sup&gt; complex</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
<th>Rh&lt;sup&gt;IV&lt;/sup&gt; complex</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>273, 336</td>
<td>6a</td>
<td>652, 927</td>
</tr>
<tr>
<td>5b</td>
<td>275, 340</td>
<td>6b</td>
<td>653, 927</td>
</tr>
<tr>
<td>5c</td>
<td>275, 338</td>
<td>6c</td>
<td>677, 937</td>
</tr>
<tr>
<td>5d</td>
<td>276, 342</td>
<td>6d</td>
<td>678, 935</td>
</tr>
<tr>
<td>5e</td>
<td>280, 309</td>
<td>6e</td>
<td>717, 970</td>
</tr>
<tr>
<td>5f</td>
<td>280, 316</td>
<td>6f</td>
<td>722, 966</td>
</tr>
</tbody>
</table>

Because the Rh<sup>IV</sup> complexes are thermally unstable at room temperature, only the most stable compound, 6f was investigated by near-IR spectroscopy (NIR spectrum of 6e observed in Figure 50 is not the spectrum of full formation resulting from low stability). As shown in Figure 50, the bands close to 970 and 1500 nm with extinction coefficients of about 2200–3500 cm<sup>-1</sup>M<sup>-1</sup> are too intense to be considered as d–d transitions. It is reasonable to assume these transitions are correlated to the charge transfer (MLCT or LMCT).

5.4 Conclusion

In summary, rare examples of air-sensitive coordinatively saturated Rh<sup>III</sup> complexes were prepared and characterized. Although oxidation of these compounds led to the thermally unstable Rh<sup>IV</sup> complexes, all the spectroscopic methods suggest that the Rh<sup>IV</sup> complexes are structurally similar to their Ir<sup>IV</sup> counterparts. These results underscore the exceptional ability of the <i>N</i>,<i>N</i>-dialkyl-<i>N</i>'<i>,N</i>''-diarylguanidinate anions to stabilize transition metals in high oxidation states and suggest them as excellent ancillary ligands for new high-valent Rh complexes that may be tailored to effect useful transformations. Current efforts are directed at the identification of the even further oxidized species detected in our electrochemical studies.
5.5 Supplemental Materials

Figure 37. $^1$H NMR spectrum of 5a.

Figure 38. $^1$H NMR spectrum of 5b.
Figure 39. $^1$H NMR spectrum of 5c.

Figure 40. $^1$H NMR spectrum of 5d.
Figure 41. $^1$H NMR spectrum of 5e.

Figure 42. $^1$H NMR spectrum of 5f.
Figure 43. Cyclic and DPV voltammograms of 0.1 mM 5a in CH₂Cl₂ (0.1 M NBu₄ClO₄) at scan rates of 0.1 V·s⁻¹.

Figure 44. Cyclic and DPV voltammograms of 0.1 mM 5b in CH₂Cl₂ (0.1 M NBu₄ClO₄) at scan rates of 0.1 V·s⁻¹.
Figure 45. Cyclic and DPV voltammograms of 0.1 mM \( \textbf{5c} \) in CH\(_2\)Cl\(_2\) (0.1 M NBu\(_4\)ClO\(_4\)) at scan rates of 0.1 V·s\(^{-1}\).

Figure 46. Cyclic and DPV voltammograms of 0.1 mM \( \textbf{5d} \) in CH\(_2\)Cl\(_2\) (0.1 M NBu\(_4\)ClO\(_4\)) at scan rates of 0.1 V·s\(^{-1}\).
Figure 47. Cyclic and DPV voltammograms of 0.1 mM $5e$ in CH$_2$Cl$_2$ (0.1 M NBu$_4$ClO$_4$) at scan rates of 0.1 V·s$^{-1}$.

Figure 48. Cyclic and DPV voltammograms of 0.1 mM $5f$ in CH$_2$Cl$_2$ (0.1 M NBu$_4$ClO$_4$) at scan rates of 0.1 V·s$^{-1}$.
Figure 49. UV−Vis spectra of 0.1 mM of 6a (—, blue), 6b (—, black), 6c (—, orange), 6d (—, red), 6e (—, purple), and 6f (—, green) in CH$_2$Cl$_2$. Pathlength = 0.5 cm.

Figure 50. Near-IR spectra of 0.1 mM of 6e (—, blue) and 6f (—, black) in CDCl$_3$. Pathlength = 1.0 cm.
CHAPTER 6

REACTIVITY OF TRIS(GUANIDINATO) COMPLEXES OF IRIDIUM AND RHODIUM

6.1 Introduction

The reactivity of Ir and Rh complexes with guanidato ligands is described in this chapter. The chemical reversibility of the Ir$^{III}$/Ir$^{IV}$ redox couple was demonstrated by adding reductants to 4a. A series of acids was utilized for investigating the p$K_a$ of 3a and 4a. As expected, compared to Ir$^{IV}$ the more electron rich Ir$^{III}$ complex, 3a, can be protonated by relatively weaker acids. Substrate oxidation was examined by reacting 4a with substrates having weak O–H or C–H bonds. The products in the oxidation of 2,4-di-$t$-butylphenol and hydroquinone were identified as 3,3',5,5'-tetra-$t$-butyl-(1,1'-biphenyl)-2,2'-diol and quinhydrone by GC-MS. A kinetic investigation was carried out for the reaction of 4a with hydroquinone. Under pseudo-first-order conditions (10–100 equiv), the observed rate constant was independent of [Ir]$_0$ and increased linearly with [hydroquinone]$_0$; $k_2 = 5.2 \cdot 10^{-4}$ M$^{-1}$·s$^{-1}$ (40 ºC). The kinetic isotopic effect (KIE = 0.9) revealed that the bond breaking is not the rate-determining step for this reaction. Values for $\Delta H^\circ$ (26.6 kcal·mol$^{-1}$) and $\Delta S^\circ$ (14.9 cal·mol$^{-1}$) were determined from reactions in the temperature range of 18–40 ºC. On the other hand, no reaction was observed for substrates having weak C–H bonds (e.g., xanthene, BDE = 75.5; 1,4-cyclohexadiene, BDE = 77.0 triphenylmethane, BDE = 81.0). Finally, substrate oxidation was also carried out by the rhodium complex, 6a, and the reactivity is much greater compared to that of the Ir counterpart 4a.
6.2 Experimental Section

**Materials.** All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Acetonitrile and dichloromethane were deoxygenated by sparging with N₂ and purified by passage through two packed columns of molecular sieves under an N₂ pressure (MBraun solvent purification system). Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using either standard Schlenk and vacuum line techniques or a glovebox. Hydroquinone was recrystallized from acetonitrile under N₂ atmosphere. 2,2,6,6-tetramethyl-piperidine-1-ol (TEMPOH) was synthesized according to a published procedure.¹¹⁵ Hydroquinone-d₂ was prepared by treating hydroquinone with degassed D₂O.

**Physical Methods.** NMR spectra were recorded on a Bruker Avance 300 or Avance DRX 400 spectrometer at ambient temperature.¹ H chemical shifts are reported in parts per million (ppm) and were referenced to residual solvent peaks. Mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source or on a double-focusing magnetic-sector Micromass, Inc., Autospec mass spectrometer using an electron impact ionization source (equipped with a solids probe). Analysis by GC–MS was performed on a TRACE GC 2000 gas chromatograph (column, DB-5 capillary) coupled with a single quadrupole ThermoFinnigan Voyager mass spectrometer with He carrier gas with a detector temperature of 250 °C and an injection temperature of 230 °C; initial temperature was maintained at 50 °C for 2 min and then raised to 250 °C at the rate of 10 °C·min⁻¹. UV–Visible spectra were recorded on an HP 8454A diode array spectrophotometer (Agilent Technologies).
Kinetic Measurements. The kinetic measurements were carried out using UV–Vis spectroscopy. A 0.1 mM solution of 4a \( (1 \times 10^{-4} \text{ mmol}) \) in 1 mL of dichloromethane was placed in a 0.5-cm UV–Vis cuvette at 40 ºC. All kinetic runs were made under pseudo-first order conditions. The progress of the reactions was monitored by following the decrease in absorbance of 4a at 696 nm. All measurements were done in triplicate, and the rate constants were obtained by linear least-squares fit to a first-order rate law.

The observed rate constants, \( k_{\text{obs}} \), were determined from reactions with a concentration of 4a of 0.1 mM and concentrations of hydroquinone in the range of 1–100 mM. \( k_{\text{obs}} \) values were also determined for reactions with a concentration of hydroquinone of 10 mM and concentrations of 4a in the range of 0.05–0.2 mM. For the Eyring analysis, measurements were performed between 18 ºC and 40 ºC.

6.3 Electron transfer

The prior study in Chapter 4 showed that the chemical oxidation of 3a–d in dichloromethane solution with [FeCp2]PF6 produced the IrIV complex, 4a–d. On the other hand, the reduction of the iridium complexes from IrIV to IrIII by mild reductants, [CoCp2] \( (E^o = −1.33 \text{ V}) \) and [Fe(C5Me5)2] \( (E^o = −0.59 \text{ V}) \),\(^{11} \) was achievable. As shown in Figure 26, one equivalent of [Fe(C5Me5)2], is required for the maximal formation of 3a. Moreover, the isosbestic point at 440 nm indicates that IrIV converts to IrIII without any formation of intermediates.

Oxidation of 3a–d was also investigated with the organic oxidants TCNE (tetracyanoethylene) \( (E^o = −0.27 \text{ V}) \) and TCNQ (tetracyanoquinodimethane) \( (E^o = −0.30 \text{ V}) \).\(^{11} \) For example, 3a–d were converted to 4a–d by treatment with 1 equiv of TCNE. However, TCNQ can only oxidize 3c and 3d.
Figure 51. Reduction of 0.1 mM 4a (—, yellow) to 3a (—, violet) in CH$_2$Cl$_2$ by addition of [FeCp*$_2$] in increments of 0.25 equiv as monitored by electronic absorption spectroscopy (pathlength, 0.5 cm). Inset: Corresponding changes of the absorbance at 362 (■, black) and 696 nm (◆, violet).

6.4 Reactivity toward Acids

A series of acids including strong acids, hydrochloric acid and trifluoromethanesulfonic acid, and acetic acid derivatives were used to evaluate the tolerance of the iridium complexes toward acids. When acetic acid ($pK_a = 4.8$),$^{129}$ 3,5-dichlorobenzoic acid ($pK_a = 3.5$),$^{129}$ iodoacetic acid ($pK_a = 3.1$),$^{129}$ and chloroacetic acid ($pK_a = 2.9$)$^{129}$ were added to 3a, no change was observed in the UV–Vis spectrum, indicating that protonation did not occur. However, when stronger acids such as dichloroacetic acid ($pK_a = 1.4$),$^{129}$ trichloroacetic acid ($pK_a = 0.7$),$^{129}$ hydrochloric acid,
or trifluoromethanesulfonic acid were added to 3a, the feature in the UV–Vis spectrum changed instantaneously (Figure 26). Interestingly, after addition of 1 equiv of TfOH to 3a, the ions representing protonation products observed in the ESI(+)MS at m/z = 908.0, 949.3, and 1140.3 are consistent with \{3a + H\}⁺, \{3a + H + MeCN\}⁺, and \{3a + 2H + 2MeCN + OTf\}⁺ (Scheme 21). The latter two ions may indicate that the guanidinato ligand was protonated, followed by conversion of bidentate to monodentate coordination and coordination of MeCN molecules to the Ir center, e.g. [Ir{L}₂{LH}(NCMe)]⁺ and [Ir{L}{LH}₂(NCMe)₂]⁺. Treatment of a second equiv of TfOH produced a new species, \{3a - L + 2 MeCN\}⁺, where L = guanidinato ligand, observed in ESI(+)MS. This ion simply reflects that the protonation occurs continuously upon addition of acids and causes removal of the guanidinato ligands.

![Graphical representation of absorbance vs. wavelength](image)

*Figure 52.* Reaction of 0.1 mM 3a with TfOH in CH₂Cl₂. Addition of [TfOH] in increments of 1 equiv as monitored by electronic absorption spectroscopy (pathlength, 0.5 cm).
On the other hand, 4a was examined by the same series of acids. Compared to 3a, 4a shows higher tolerance toward strong acid TfOH (Figure 58). Likewise, no change of feature was observed when using 1–5 equiv of acetic acid, 3,5-dichlorobenzoic acid, iodoacetic acid, and chloroacetic acid. Unlike 3a, 4a does not react with dichloroacetic acid, and reacted slowly with 2 equiv of trichloroacetic acid, which indicates that 4a has weaker affinity toward protons than 3a because of its higher oxidation state of the metal center.

Scheme 21. Protonation of 3a with Acid.

6.5 Reactivity toward Organic Substrates with O–H bonds

6.5.1 Reactivity of Iridium(IV) Complexes

In order to understand the reactivity of IrIV complexes, different types of substrates with C–H and O–H bond were investigated. First, the reaction with the O–H bond substrates was examined.

The reaction with 2,4-di-tert-butylphenol only occurred slowly at higher temperature (40 °C) and larger excess (>1000 equiv). Although TEMPOH would be a
good substrate (10 equiv, 20 °C: $t_{1/2} = 1700$ s; 10 equiv, 40 °C: Ir$^{IV}$ $t_{1/2} = 200$ s) in terms of reaction time and amount of substrate used, the kinetic decay curve suggests that the reaction may not follow a simple first- or second-order rate law. Hydroquinone was a suitable candidate for the oxidative chemistry with Ir$^{IV}$ complexes. Addition of 10 or more equiv of hydroquinone to 0.1 mM of 4a in CH$_2$Cl$_2$ at 40 °C resulted in formation of the charge transfer complex, quinhydrone, which was observed in the GC–MS. Although the inorganic products were not observed by mass spectroscopy, the final UV–Vis spectrum of the reaction was similar to the spectrum obtained from protonation of 3a, which indicates that after oxidation of hydroquinone, a free proton was released causing the protonation of the Ir complex.

Figure 53. Reaction of 0.1 mM 4a with 100 equiv of hydroquinone in CH$_2$Cl$_2$ at 40 °C as monitored by electronic absorption spectroscopy. Inset: Time course of the reactions of 4a ($\lambda = 696$ nm). Pathlength = 0.5 cm.
Figure 54. First-order rate law fit (solid line) for the reaction (♦) of 0.1 mM 4a with 100 equiv of hydroquinone in CH₂Cl₂ at 40 °C as monitored by electronic absorption spectroscopy. Pathlength = 0.5 cm.

Time courses for six different concentrations (1, 4, 10, 20, 40, and 60 mM) of hydroquinone (under pseudo-first-order conditions) at 40 °C were investigated to determine the reaction order in hydroquinone (Figure 27). The half-lives decrease with increasing [HQ], and the time courses fit to a first-order rate law (Figure 28). It was found that experimental plots of ln[A] vs. t appeared to be approximately linear over three half-lives, and the $k_{obs}$ values were in the range of $2.4 \cdot 10^{-4}$ to $2.0 \cdot 10^{-2}$ s$^{-1}$ and increase linearly with [HQ] (Figure 29). In a similar manner, the time courses for five different concentrations (0.05, 0.07, 0.1, 0.14, and 0.2 mM) of 4a under pseudo-first-order conditions at 40 °C were observed (Figure 59). The half-lives are constant with varying [4a], and the time courses fit to a first-order rate law. The plots of ln[A] vs. t appear to be approximately linear over three half-lives and the $k_{obs}$ values were found to be independent of [4a]. As a result, the second-order rate constant, $k_2 = 3.2 \cdot 10^{-4}$ M$^{-1}$s$^{-1}$, was determined from the slope of a plot of $k_{obs}$ vs. [HQ]. An inverse kinetic isotopic
effect (KIE = 0.9) suggests that the O–H(D) bond breaking is not the rate-determining step in the reaction (Figure 60). It is worth noting that the reaction was accelerated in the presence of trifluoromethanesulfonic acid, and the half-lives (145 to 15 s) decrease with increasing [TfOH] (1 to 4 equiv, Figure 61). Additionally, the reaction could also be sped up ($t_{1/2} = 160$ s) in the presence of 1 equiv of pyridine under the same reaction conditions (100 equiv of hydroquinone at 40 °C, Figure 62).

Figure 55. The plot of $k_{obs}$ vs. [HQ] for the reaction of 0.1 mM 4a with variable concentration of hydroquinone.

The Eyring plot for the reduction of 4a by hydroquinone in dichloromethane over the temperature range of 18 to 40 °C is shown in Figure 30. A linear fit of ln($k_{obs}/T$) vs. $1/T$ was used to determine the enthalpy ($\Delta H^\neq$) and entropy ($\Delta S^\neq$) of activation. The $\Delta H^\neq$ and $\Delta S^\neq$ were determined to be 26.6 kcal·mol$^{-1}$ and 14.9 cal·mol$^{-1}$, respectively.
As anticipated, because the metal center is well protected by the bulky tris-ligand environment, the oxidation of hydroquinone is impossible through an inner-sphere mechanism, since no coordination site is available. In addition, the outer-sphere electron transfer was ruled out as well, considering the oxidation potential of 4a is not strong enough to oxidize the organic substrates mentioned above. Therefore, the possible reaction mechanisms for the O–H bond substrate oxidation with IrIV complex were shown in Figure 31: a) the interaction of IrIV complex with organic substrate through hydrogen bonding followed by electron transfer; b) the protonation of IrIV complex occurred with the O–H organic substrate followed by opening a coordination site, binding with organic substrate, and transferring electron from substrates to metal center. Given the pKₐ values of IrIV complex and organic substrates, the pathway (b) must be eliminated because the protonation evaluation (Section 6.4) shows that strong acids are
required to protonate IrIV complex. The interaction of IrIV complex with the O–H organic substrate through hydrogen bonding described in pathway (a) may be a key step for proceeding the reaction. This may be explained that no reaction occurred when using substrates with C–H bonds. In addition, the fact that the reaction can be accelerated by addition of acids can also elucidate that the open coordination site is crucial for the reaction.

Figure 57. The proposed mechanism for the substrate oxidation of IrIV complexes

Likewise, while complexes 4b–d also reacted with hydroquinone, the rates of the reactions varied with the substituents on the guanidinato ligand. Rate constants ($k_2$) for four different concentrations (4, 10, 40, and 60 mM) of hydroquinone (under pseudo-first-order conditions) at 40 °C were investigated to determine the reaction order in hydroquinone (Figures 63–65). Under the same conditions, the $k_2$ of the IrIV complexes decrease in the expected order 4a < 4b < 4c < 4d ($k_2 = 3.2 \cdot 10^{-4}, 8.2 \cdot 10^{-5}, 6.8 \cdot 10^{-5},$
and 7.0 x 10⁻⁶ s respectively). The linear correlation between Ir⁺⁺/⁺ redox potentials and the half-lives of the corresponding Ir⁺⁺⁺ complexes may indicate that the rate determining step of the hydroquinone oxidation is the electron-transfer process.

Although the reaction with substrates possessing weaker C–H bonds (e.g. 1,4-cyclohexadiene, triphenylmethine, dihydroanthracene, and xanthene) did not occur, the transformation could be observed with the O–H bond substrate such as TEMPOH, 2,4-di-tert-butylphenol, and hydroquinone. Therefore, bond dissociation energy of the C–H/O–H is not the only factor that affects the reaction; another factor, pKₐ value of C–H/O–H, also plays a major role in the substrate oxidation.

6.5.2 Reactivity of Rhodium(IV) Complexes

The reactivity of Rh⁺⁺⁺ complexes is expected to be higher than their Ir⁺⁺⁺ counterparts, because they have higher redox potentials (as described in Chapter 5). Due to thermal instability, all the reactions for 6a must be carried out at −60 °C. However, even at low temperature 6a is still highly reactive toward substrates with O–H bonds. For example, the t₁/₂ for the reaction of 6a with 100 equiv of 2,4-di-tert-butylphenol at −60 °C is ca. 1 hour, and the t₁/₂ for reaction of 4a with 1000 equiv of 2,4-di-tert-butylphenol at room temperature is ca. 3.3 hours. Therefore, the Rh⁺⁺⁺ complexes should be good oxidants for the oxidation of substrates with O–H bond.

6.6 Conclusion

The reactivity studies suggest that the tris(guanidinato)iridium(III) and tris(guanidinato)iridium(IV) complexes can undergo a variety of reactions. First, the reversibility of Ir⁺⁺⁺/⁺ observed in electrochemical studies can be carried out through chemical oxidation and reduction. The protonation of Ir⁺⁺⁺ and Ir⁺⁺⁺⁺ complexes not only evaluates the approximate pKₐ values for both complexes but also demonstrates that the
electron deficient Ir^{IV} complexes have less affinity toward acids than that of Ir^{III}. Kinetic measurements show that the overall reaction is second order, and the kinetic isotope effect study suggests that the O–H bond breaking is not the rate determining step. The outer-sphere and inner-sphere electron transfer mechanism would be ruled out considering the large gap of redox potential between Ir^{IV} complexes and substrates, and the coordinatively saturated nature of the Ir^{IV} complexes. The addition of acid, which will open a coordination site, causes acceleration of the reaction.

Therefore, all the evidence from the experiments suggests that opening a coordination site on coordinatively saturated Ir^{IV} complexes is a key step for the substrate oxidation reaction. Finally, the reactivity of substrate oxidation for Rh^{IV} complexes is found to be higher than that of the Ir^{IV} counterpart.

6.7 Supplemental Materials

*Figure 58.* Reaction of 0.1 mM 4a with TfOH in CH₂Cl₂. Addition of [TfOH] in increments of 1 equiv as monitored by electronic absorption spectroscopy (pathlength, 0.5 cm).
Figure 59. The plot of $k_{obs}$ vs. [Ir] for the reaction of 10 mM hydroquinone with variable concentration of 4a.

Figure 60. The plot of $k_{obs}$ vs. [HQ-$d_2$] for the reaction of 0.1 mM 4a with variable concentration of hydroquinone-$d_2$. 
Figure 61. Reaction of 0.1 mM 4a with 100 equiv of hydroquinone in the presence of 3 equiv of HOTf in CH$_2$Cl$_2$ at 40 °C as monitored by electronic absorption spectroscopy. Inset: Time course of the reactions of 4a (λ = 696 nm). Pathlength = 0.5 cm.

Figure 62. Reaction of 0.1 mM 4a with 100 equiv of hydroquinone in the presence of 1 equiv of pyridine in CH$_2$Cl$_2$ at 40 °C as monitored by electronic absorption spectroscopy. Inset: Time course of the reactions of 4a (λ = 696 nm). Pathlength = 0.5 cm.
Figure 63. Reaction of 0.1 mM 4b with 100 equiv of hydroquinone in CH$_2$Cl$_2$ at 40 °C as monitored by electronic absorption spectroscopy. Inset: The plot of $k_{\text{obs}}$ vs. [HQ] for the reaction of 0.1 mM 4b with variable concentration of hydroquinone. Pathlength = 0.5 cm.

Figure 64. Reaction of 0.1 mM 4c with 100 equiv of hydroquinone in CH$_2$Cl$_2$ at 40 °C as monitored by electronic absorption spectroscopy. Inset: The plot of $k_{\text{obs}}$ vs. [HQ] for the reaction of 0.1 mM 4c with variable concentration of hydroquinone. Pathlength = 0.5 cm.
Figure 65. Reaction of 0.1 mM 4d with 100 equiv of hydroquinone in CH₂Cl₂ at 40 °C as monitored by electronic absorption spectroscopy. Inset: The plot of $k_{obs}$ vs. [HQ] for the reaction of 0.1 mM 4d with variable concentration of hydroquinone. Pathlength = 0.5 cm.
Mononuclear complexes of a low-valent \( d \)-block metal center coordinated by bidentate guanidinato(1–) ligands were prepared and characterized, thereby expanding the scope of this ligand platform in transition-metal chemistry. Spectroscopic evidence suggests that the \( N,N \)-dialkyl-\( N',N'' \)-diarylguanidinates employed here function as stronger donors than other monoanionic, nitrogen-based scaffolds, such as tris(pyrazolyl)borates-\( \kappa^2 \) and \( \beta \)-diketiminates, when bound to the Ir\(^{1}(\text{coe})_2 \) unit. The reaction of complexes 2\( \text{a–c} \) with O\(_2\) led to product mixtures in which tris(chelate)iridium(III) complexes could be identified. This observation suggested a method for the rational synthesis of such complexes.

Rare examples of air-sensitive coordinatively saturated Ir\(^{\text{III}}\) and Rh\(^{\text{III}}\) complexes were prepared and characterized. Oxidation of the Ir compounds produced isolable, stable tris(guanidinato)iridium(IV) complexes, in which the Ir center is exclusively coordinated by nitrogen-donor ligands. For the Rh counterparts, oxidation generated thermally unstable tris(guanidinato)rhodium(IV) complexes. These results underscore the exceptional ability of the \( N,N \)-dialkyl-\( N',N'' \)-diarylguanidinate anions to stabilize transition metals in high oxidation states and suggest them as excellent ancillary ligands for new high-valent Ir and Rh complexes that may be tailored to effect useful transformations. Finally, the reactivity studies show that the high-valent complexes can oxidize substrates with O–H bonds.

Several directions related to this work can approach in the future. First, as observed in the cyclic voltammograms of 3\( \text{a–d} \) in Figure 12 and Figures 26–28, the second redox process points at the existence of a doubly oxidized. Such compounds would be of interest because of their highly oxidizing power. However, they may be
expected to be fairly unstable so that the attempt synthesis and characterization may be carried out *in situ* at low temperature. Spectroscopic characterization could provide insights into their electronic structure and help answer the question whether those species are Ir$^V$ or Ir$^{IV}$–ligand-radical complexes.

Secondly, the ability of the tris(guanidinato) platform to stabilize often transition metal centers in high oxidation states could be tested. For example, to complete the systematic investigation for the Group 9 of the periodic table, the cobalt tris(guanidinato) analogues can be prepared and characterized. Once the tris(guanidinato)cobalt(III) were prepared, the exploration of even rare Co$^{IV}$ will be intriguing.
APPENDIX

TETRADENTATE PYRIDYL/BENZIMIDAZOYL LIGANDS AND IRON(II) AND OXOIIRON(IV) COMPLEXES

A.1 Introduction

Two tetradeinate ligands L1 and L2, and their FeII complexes, [Fe(L1)(OTf)2] and [Fe(L2)(OTf)2]; where L1 = N,N-bis(2-benzimidazolylmethyl)-N-(2-pyridylmethyl)amine and L2 = N,N-bis[(1-methylbenzimidazol-2-yl)methyl]-N-[(pyridin-2-yl)methyl]amine; were synthesized and characterized. The Fe−N bond lengths in the complexes obtained from solid state structures suggest that the Fe center in [Fe(L1)(NCMe)2](OTf)2 is low-spin (S = 0) and that in [Fe(L2)(NCMe)2](OTf)2 is high-spin (S = 2). However, the 1H NMR spectra of these compounds in CD3CN solution both exhibit paramagnetically shifted peaks between 120 and −15 ppm, which are typical for high-spin FeII complexes. The spin states of [Fe(L1)(NCMe)2]2+ in solution was further investigated by variable-temperature (VT) NMR spectroscopy. VT 1H NMR spectroscopy (−40 to +80 °C) for [Fe(L1)(NCMe)2]2+ shows the spin equilibrium between high-spin and low-spin states over the temperature range of −40 to +50 °C. In addition, oxoiiron(IV) complexes can be generated by reacting FeII complexes with excess of mCPBA at −40 °C. It is found that [FeIV(O)(L1)(NCMe)2](OTf)2 and [FeIV(O)(L2)(NCMe)2](OTf)2 are highly unstable in solution at −40 °C, where the former displays greater stability. The series studies of stability of [FeIV(O)(L)(NCMe)2](OTf)2, where L = tris (pyridylmethyl)amine, L1, L2, and tris(2-benzimidazolylmethyl)amine; suggest that the stability of these FeIV=O complexes varies with the pendant arm of the tetradeinate ligands.
A.2 Experimental Section

Materials and Physical Methods. All reagents and solvents were purchased from commercial sources and were used as received, unless noted otherwise. Acetonitrile, dichloromethane, diethyl ether, and tetrahydrofuran were deoxygenated by sparging with N$_2$ and purified by passage through two packed columns of molecular sieves under an N$_2$ pressure (MBraun solvent purification system). Nitromethane was refluxed over CaH$_2$ under an Ar atmosphere, distilled, and passed through a column of basic Al$_2$O$_3$. $m$-Chloroperbenzoic acid was purified by dissolving in benzene and washing with a pH 7.4 phosphate solution. The organic phase was dried over MgSO$_4$, evaporated under reduced pressure, and the residue was recrystallized from dichloromethane. Preparation and handling of air- and moisture-sensitive materials were carried out under an inert gas atmosphere by using either standard Schlenk and vacuum line techniques or a glovebox. Fe(OTf)$_2$·2MeCN$^{116}$ was synthesized by a modified literature method$^{117}$ from anhydrous FeCl$_2$ and trimethylsilyl trifluoromethanesulfonate in acetonitrile and recrystallized from acetonitrile–diethyl ether.$^{118} \text{[Fe(Me}_3\text{ntb)}(\text{OTf)}_2\text{]}$ was received from professor Wonwoo Nam’s research group in the Ewha Womans University, Korea. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA, USA.

NMR spectra were recorded on a Bruker Avance MicroBay 300, Avance DPX 300, and Avance DRX 400. VT-NMR spectra were recorded on Bruker Avance DRX 400 in the temperature range of $−40$ to $+80$ °C. $^1$H chemical shifts are reported in parts per million (ppm) and were referenced to residual solvent peaks. Mass spectral data were acquired on a quadrupole ion trap ThermoFinnigan LCQ Deca mass spectrometer using an electrospray ionization source. UV–Visible spectra were recorded on an HP 8453A diode array spectrophotometer (Agilent Technologies) with samples maintained at low temperature using a cryostat from Unisoku Scientific Instruments, Japan.
**2-Benzimidazolylmethylamine.** A solution of 3.30 g (44.0 mmol) of glycine and 4.75 g (43.9 mmol) of 1,2-diaminobenzene in 20 mL of 7 M HCl was heated under reflux for three days. When the solution was cooled to room temperature, the product precipitated in form of its hydrochloride salt. The precipitate was separated by filtration and dissolved in 20 mL of water, followed by addition of an NH₄OH solution to adjust the pH to 9. The solution was washed with dichloromethane (2 x 10 mL). The product, which is more soluble in water than in dichloromethane, was obtained in crystalline form by storing the aqueous solution at ca. 4 °C. Yield: 4.61 g (71%). ¹H NMR (300 MHz, D₂O, δ): 7.59-7.56 (m, 2H, Ar H), 7.30-7.27 (m, 2H, Ar H) 4.35 (s, 2H, CH₂NH₂).

**N-(2-Benzimidazolylmethyl)-N,N-bis(2-pyridylmethyl)amine.** This compound was synthesized by a modified literature method. A suspension of 3.90 g (23.8 mmol) of 2-(chloromethyl)pyridine hydrochloride and 1.04 g (7.07 mmol) of 2-benzimidazolylmethylamine in 50 mL of dichloromethane was prepared at 0 °C. A solution of 7.7 mL (5.6 g, 55 mmol) of triethylamine in 20 mL of dichloromethane was added dropwise to this suspension under stirring, after which the resulting mixture was allowed to warm to room temperature and stirred for three days. The reaction mixture was washed with 50 mL of water and dried over MgSO₄. The solvent was removed under reduced pressure to afford a red oil, which was washed with 50 mL of diethyl ether to remove excess 2-(chloromethyl)pyridine and dissolved in 50 mL of dichloromethane. The solution was washed with water (3 x 30 mL) and dried over MgSO₄. The solvent was removed under reduced pressure to give a brown solid. This product was used without further purification in the next step. Yield: 0.71 g (31%). ¹H NMR (300 MHz, CDCl₃, δ): 8.63 (m, 2H, Ar H), 7.64-7.59 (m, 4H, Ar H), 7.32 (d, 2H, Ar H), 7.24-7.17 (m, 4H, Ar H), 4.09 (s, 2H, benzimidazolyl CH₂N), 3.91 (s, 4H, pyridyl CH₂N).

**N-[(1-Methylbenzimidazol-2-yl)methyl]-N,N-bis[(pyridin-2-yl)methyl]amine (L1).** To 88 mg (1.57 mmol) of powdered KOH (prepared under exclusion of moisture)
were added a solution of 170 mg (0.52 mmol) of \(N\)-(2-benzimidazolylmethyl)-\(N,N\)-bis(2-pyridylmethyl)amine in 10 mL of dimethyl sulfoxide and 0.049 mL (0.11 g, 0.79 mmol) of iodomethane. The reaction mixture was stirred for 1 h, after which it was poured into 50 mL of water. The product was extracted with chloroform (3 x 30 mL), and the combined organic phases were washed with water (5 x 30 mL) and dried over MgSO\(_4\). The volatiles were removed under reduced pressure to afford an orange solid. The product was extracted from the residue with 100 mL of diethyl ether and, after evaporation of the solvent, isolated as a yellow solid. The product was recrystallized from acetone and dried in vacuo. Yield: 103 mg (58%). Anal. Calcd for C\(_{21}\)H\(_{21}\)N\(_5\): C, 73.44; H, 6.16; N, 20.39. Found: C, 72.98; H, 6.11; N, 20.46. \(^1\)H NMR (300 MHz, CDCl\(_3\), \(\delta\)): 8.54 (m, 2H, Ar H), 7.70 (m, 1H, Ar H), 7.60 (m, 2H, Ar H), 7.39 (d, \(J = 7.8\) Hz, 2H, Ar H), 7.26-7.10 (m, 5H, Ar H), 4.02 (s, 2H, benzimidazolyl CH\(_2\)N), 3.88 (s, 4H, pyridyl CH\(_2\)N), 3.69 (s, 3H, NCH\(_3\)). \(^{13}\)C NMR (75.5 MHz, CDCl\(_3\), \(\delta\)): 158.5, 151.6, 149.1, 143.1, 136.2, 123.6, 122.4, 122.1, 121.7, 119.6, 109.0, 60.3 (pyridyl CH\(_2\)N), 51.3 (benzimidazolyl CH\(_2\)N), 30.0 (NCH\(_3\)). EIMS (70 eV) \(m/z\): M\(^{+}\) calcd for C\(_{21}\)H\(_{21}\)N\(_5\), 343.18; found, 343.0.

**Dipotassium \(N\)-(2-pyridylmethyl)iminodiacetate.**\(^{120}\) To a stirred solution of 1.33 g (10.0 mmol) of iminodiacetic acid and 1.12 g (20.0 mmol) of KOH in 10 mL of water, which was kept in an ice bath, was added dropwise a solution of 1.64 g (10.0 mmol) of 2-(chloromethyl)pyridine hydrochloride and 0.56 g (10.0 mmol) of KOH in 10 mL of water. Subsequently, 0.69 g (4.99 mmol) of K\(_2\)CO\(_3\) was added, and the solution was stirred at 80 °C for 18 h. The volatiles were removed under reduced pressure. The residue was taken up in 10 mL of methanol, the solution was filtered, and the maroon filtrate was evaporated to dryness. Yield: 1.61 g (54%). \(^1\)H NMR (300 MHz, D\(_2\)O, \(\delta\)): 8.41 (d, \(J = 4.8\) Hz, 1H, Ar H), 7.80 (t, \(J = 6.5\) Hz, 1H, Ar H), 7.53 (d, \(J = 7.8\) Hz, 1H, Ar H), 7.31 (t, \(J = 7.5\) Hz, 1H, Ar H), 3.95 (s, 2H, pyridyl CH\(_2\)N), 3.28 (s, 4H, NCH\(_2\)CO\(_2\)K).
**N,N-Bis(2-benzimidazolylmethyl)-N-(2-pyridylmethyl)amine.** A solution of 1.98 g (6.60 mmol) of dipotassium N-(2-pyridylmethyl)iminodiacetate and 1.44 g (13.3 mmol) of 1,2-diaminobenzene in 140 mL of 6 M HCl was heated under reflux for three days. Heating was briefly interrupted to add activated carbon, and the solution was heated under reflux for another 10 min. Subsequently, the solution was filtered and treated with an NH₄OH solution (to adjust the pH to 9), which resulted in the formation of a precipitate. The precipitate was separated by filtration and dissolved in 30 mL of chloroform. The organic solution was washed with an aqueous 0.1 M NaOH solution (3 x 20 mL), dried over MgSO₄ and evaporated to dryness. The crude product was purified by column chromatography on silica gel using a solution of 1% NEt₃ in acetone as the eluent to afford a brown solid. Yield: 0.26 g (11%). ¹H NMR (300 MHz, CDCl₃, δ): 8.46 (d, J = 3.5 Hz, 1H, Ar H), 7.58-7.55 (m, 4H, Ar H), 7.41 (m, 1H, Ar H), 7.26-7.17 (m, 5H, Ar H), 7.05-7.03 (m, 1H, Ar H), 4.04 (s, 4H, benzimidazolyl CH₂N), 3.85 (s, 2H, pyridyl CH₂N).

**N,N-Bis[(1-methylbenzimidazol-2-yl)methyl]-N-[(pyridin-2-yl)methyl]amine (L2).** To 200 mg (3.56 mmol) of powdered KOH (prepared under exclusion of moisture) were added a solution of 220 mg (0.60 mmol) of N,N-bis(2-benzimidazolylmethyl)-N-(2-pyridylmethyl)amine in 10 mL of DMSO and 0.11 mL (0.25 g, 1.77 mmol) of iodomethane. The reaction mixture was stirred for 1 h, after which it was poured into 50 mL of water. The product was extracted with chloroform (3 x 40 mL), and the combined organic phases were washed with water (5 x 40 mL) and dried over MgSO₄. The volatiles were removed under reduced pressure to afford a red solid. The crude product was washed with acetone to afford a yellow solid, which was recrystallized from dichloromethane and dried *in vacuo*. Yield: 152 mg (64%). Anal. Calcd for C₂₄H₂₄N₆: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.16; H, 5.99; N, 21.06. ¹H NMR (300 MHz, CDCl₃, δ): 8.56 (m, 1H, Ar H), 7.73 (m, 2H, Ar H), 7.57 (m, 1H, Ar H), 7.27-7.13 (m, 8H, Ar H), 4.09 (s, 4H, benzimidazolyl CH₂N), 3.95 (s, 2H, pyridyl CH₂N), 3.49 (s, 6H,
NCH₃). ¹³C NMR (75.5 MHz, CDCl₃, δ): 157.7, 151.2, 149.1, 142.2, 136.3, 136.0, 124.3, 122.6, 122.3, 121.9, 119.6, 109.0, 60.2 (pyridyl CH₂N), 50.8 (benzimidazolyl CH₂N), 29.5 (NCH₃). EIMS (70 eV) m/z: M⁺ calcd for C_{24}H_{24}N₆, 396.21; found, 396.3.

[Fe(L1)(OTf)₂]. A solution of 436 mg (1.00 mmol) of Fe(OTf)₂·2MeCN in 10 mL of tetrahydrofuran was added to a stirred solution of 350 mg (1.02 mmol) of L1 in 10 mL of tetrahydrofuran under an N₂ atmosphere. The resulting solution was stirred for 3 h. The solution was concentrated to a volume of 2 mL, and 10 mL of diethyl ether was added to cause the product to precipitate. The product was separated by filtration and recrystallized by vapor diffusion of diethyl ether into a nitromethane solution of the product at −30 °C to yield pale yellow single crystals. The crystalline solid was dried in vacuo. Yield: 495 mg (71%). Anal. Calcd for C_{23}H_{21}F₆FeN₅O₆S₂: C, 39.61; H, 3.04; N, 10.04; S, 9.20. Found: C, 39.87; H, 3.24; N, 9.76; S, 9.23. ¹H NMR (300 MHz, CD₃CN, δ): 83.1 (br, 2H, pyridyl Ar H), 68.7, (br, 2H, pyridyl CH₂N), 65.8 (br, 2H, pyridyl CH₂N), 56.8 (br, 2H, benzimidazolyl CH₂N), 46.7 (s, 2H, pyridyl Ar H), 42.8 (s, 2H, pyridyl Ar H), 25.0 (s, 1H, benzimidazolyl Ar H), 15.7 (s, 1H, NCH₃) 5-0 (2H, benzimidazolyl Ar H), −4.7 (br, 1H, benzimidazolyl Ar H), −7.8 (s, 2H, pyridyl Ar H). ESI(+)MS (MeNO₂) m/z: M⁺ calcd for C_{22}H_{21}F₃FeN₅O₃S ([Fe(L1)(OTf)]⁺), 548.07; found, 548.1. Upon dissolution in acetonitrile, [Fe(L1)(OTf)₂] was converted into [Fe(L1)(NCMe)₂](OTf)₂. UV–Vis (MeCN) λ_max, nm (ε): 375 (1200), 495 (70). Red single crystals of X-ray diffraction quality were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the product at −30 °C.

[Fe(L2)(OTf)₂]. A solution of 436 mg (1.00 mmol) of Fe(OTf)₂·2MeCN in 10 mL of tetrahydrofuran was added to a stirred suspension of 404 mg (1.02 mmol) of L2 in 10 mL of tetrahydrofuran under an N₂ atmosphere. The reaction mixture was stirred for 3 h. The mixture was concentrated to a volume of 2 mL and 10 mL of diethyl ether were added. The precipitate was separated by filtration, and the residue was recrystallized by vapor diffusion of diethyl ether into a nitromethane solution of the product at −30 °C.
Colorless single crystals were obtained and dried in vacuo. Yield: 596 mg (79%). Anal. Calcd for C₁₂₆H₁₂₄F₆Fe₆N₆O₆S₂: C, 41.61; H, 3.22; N, 11.20; S, 8.55. Found: C, 40.80; H, 3.19; N, 10.95; S, 8.67. ¹H NMR (300 MHz, CD₃CN, δ): 118.1 (br, 1H, pyridyl Ar H), 99.6, (br, 2H, pyridyl CH₂N), 76.7 (br, 2H, benzimidazolyl CH₂N), 72.3 (br, 2H, benzimidazolyl CH₂N), 55.0 (s, 1H, pyridyl Ar H), 53.5 (s, 1H, pyridyl Ar H), 29.2 (s, 2H, benzimidazolyl Ar H), 19.9 (s, 6H, NCH₃) 5-0 (4H, benzimidazolyl Ar H), −4.8 (br, 2H, benzimidazolyl Ar H), −13.2 (s, 2H, pyridyl Ar H). ESI(+)MS (MeNO₂) m/z: M⁺ calcd for C₂₅H₂₄F₃Fe₆N₆O₃S ([Fe(L₂)(OTf)]⁺), 601.09; found, 601.1. Upon dissolution in acetonitrile, [Fe(L₂)(OTf)₂] was converted into [Fe(L₂)(NCMe)₂](OTf)₂. UV−Vis (MeCN) λₘₐₓ, nm (ε): 360 (1000), 490 (80). Pale yellow crystals of X-ray diffraction quality were obtained by vapor diffusion of di ethyl ether into an acetonitrile solution of the product at −30 °C.

**Reaction of [Fe(L₁)(OTf)₂] and [Fe(L₂)(OTf)₂] with mCPBA.** Both Fe^{IV}=O species were prepared according to the general procedure outlined below. A 1 mL solution of 1 mM Fe^{II} complex in acetonitrile was cooled to −40 °C, then 3 equiv of mCPBA in acetonitrile were added to this cold solution. The greenish intermediate which forms immediately upon addition of mCPBA was monitored by UV−Vis spectroscopy. UV−Vis (MeCN) λₘₐₓ, nm (ε): 733 (230) for [Fe(L₁)(OTf)₂] and 747 (220) for [Fe(L₂)(OTf)₂].

**Reaction of [Fe(L₁)(OTf)₂] and [Fe(L₂)(OTf)₂] with AcOOH.** Both Fe^{IV}=O species could also be prepared by using peracetic acid with slightly lower yield. A 1 mL solution of 1 mM Fe^{II} complex in acetonitrile was cooled to −40 °C, and then 5 equiv of AcOOH in acetonitrile were added to this cold solution. The greenish intermediate which forms immediately upon addition of AcOOH was used for ESI mass spectroscopic measurements. Although higher yields were obtained with mCPBA according to UV−Vis spectroscopy, the ESI mass spectra were not satisfactory. Therefore, all the Fe^{IV}=O species monitored by ESI mass spectrometry were generated by peracetic acid. For
[Fe(L1)(OTf)2], ESI(+)MS m/z: M⁺ calcd for C22H21F3FeN5O4S, 564.04; found, 563.9
{[Fe(L1)(OTf)] + O}⁺, 227.9 {[Fe(L1)] + O + MeCN}²⁺, 207.8 {[Fe(L1)] + O}²⁺; For
[Fe(L2)(OTf)2], ESI(+)MS m/z: M⁺ calcd for C25H24F3FeN6O4S, 617.09; found, 616.9
{[Fe(L2)(OTf)] + O}⁺, 254.5 {[Fe(L2)] + O + MeCN}²⁺, 234.6 {[Fe(L2)] + O}²⁺.

X-ray Crystallographic Analyses. A single crystal of each compound was
coated with Paratone N oil and mounted on a glass capillary for data collection at 190(2)
K for [Fe(L1)(NCMe)2](OTf)2 and 210(2) K for [Fe(L2)(NCMe)2](OTf)2 on a Nonius
KappaCCD diffractometer using Mo Kα radiation (graphite monochromator). The
temperature was controlled by an Oxford Cryostream Cooler (700 series, N₂ gas). Data
collection, data reduction, and absorption correction were carried out following standard
CCD techniques using the software packages Collect and HKL-2000. Final cell
constants were calculated from 5312 ([Fe(L1)(NCMe)2](OTf)2) or 6279
[Fe(L2)(NCMe)2](OTf)2 reflections from the complete data set. The space groups P−1
([Fe(L1)(NCMe)2](OTf)2) and P−1 ([Fe(L2)(NCMe)2](OTf)2) were determined based on
systematic absences and intensity statistics. The structures were solved by direct methods
and refined by full-matrix least-squares minimization and difference Fourier methods
(SHELXTL v.6.12). All non-hydrogen atoms were refined with anisotropic
displacement parameters. Severe disorder of the triflate anion in both complexes led to a
less satisfactory R values, but the cations in both compounds are well defined. In
[Fe(L1)(NCMe)2](OTf)2, one of the two triflate anions was modelled with two
components (74.0:26.0). The final full-matrix least-squares refinement converged to R1 =
0.222 and wR2 = 0.230 [F², all data]. For [Fe(L2)(NCMe)2](OTf)2, the final full-matrix
least-squares refinement converged to R1 = 0.103 and wR2 = 0.190 [F², all data]. Table
A1 contains additional crystal and refinement information. Selected distances and angles
are summarized in Tables A2 and A3.
Table A1. Crystallographic data and structure refinement for [Fe(L1)(NCMe)2](OTf)2, and [Fe(L2)(NCMe)2](OTf)2.

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<td>1645.0(4) Å³</td>
<td>1804.9(3) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density</td>
<td>1.574 Mg·m⁻³</td>
<td>1.532 Mg·m⁻³</td>
</tr>
<tr>
<td>Absorption coefficient, μ</td>
<td>0.671 mm⁻¹</td>
<td>0.618 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>796</td>
<td>852</td>
</tr>
<tr>
<td>θ range for data collection</td>
<td>3.13 to 25.28°</td>
<td>2.85 to 25.37°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>−14 ≤ h ≤ 14, −15 ≤ k ≤ 15, −15 ≤ l ≤ 15</td>
<td>−14 ≤ h ≤ 14, −15 ≤ k ≤ 15, −15 ≤ l ≤ 15</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>10922 / 5903 [R(int) = 0.1087]</td>
<td>12094 / 6577 [R(int) = 0.0306]</td>
</tr>
<tr>
<td>Completeness to θ</td>
<td>98.8 % (θ = 25.28°)</td>
<td>99.2 % (θ = 25.37°)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5903 / 20 / 464</td>
<td>6577 / 0 / 482</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.032</td>
<td>1.030</td>
</tr>
<tr>
<td>Final R indices [I &gt; 2σ(I)]</td>
<td>R1 = 0.0969, wR2 = 0.1813</td>
<td>R1 = 0.0660, wR2 = 0.1656</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.2216, wR2 = 0.2296</td>
<td>R1 = 0.1026, wR2 = 0.1901</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.576 and -0.357 e·Å⁻³</td>
<td>0.953 and -0.566 e·Å⁻³</td>
</tr>
</tbody>
</table>
Table A2. Selected interatomic distances (Å) for [Fe(L1)(NCMe)2](OTf)2 and [Fe(L2)(NCMe)2](OTf)2.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th><a href="OTf">Fe(L1)(NCMe)2</a>2</th>
<th><a href="OTf">Fe(L2)(NCMe)2</a>2</th>
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</thead>
<tbody>
<tr>
<td>Fe–N1</td>
<td>2.019(6)</td>
<td>2.296(4)</td>
</tr>
<tr>
<td>Fe–N2</td>
<td>1.967(6)</td>
<td>2.177(4)</td>
</tr>
<tr>
<td>Fe–N3</td>
<td>1.992(6)</td>
<td>2.142(3)</td>
</tr>
<tr>
<td>Fe–N5</td>
<td>1.976(6)</td>
<td>2.115(4)</td>
</tr>
<tr>
<td>Fe–N6</td>
<td>1.966(7)</td>
<td>2.198(4)</td>
</tr>
<tr>
<td>Fe–N7</td>
<td>1.924(8)</td>
<td>2.127(4)</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figures A5 and A6.

Table A3. Selected interatomic angles (°) for [Fe(L1)(NCMe)2](OTf)2 and [Fe(L2)(NCMe)2](OTf)2.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th><a href="OTf">Fe(L1)(NCMe)2</a>2</th>
<th><a href="OTf">Fe(L2)(NCMe)2</a>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(7)-Fe-N(6)</td>
<td>88.8(3)</td>
<td>111.65(15)</td>
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<tr>
<td>N(7)-Fe-N(2)</td>
<td>95.8(3)</td>
<td>86.94(13)</td>
</tr>
<tr>
<td>N(6)-Fe-N(2)</td>
<td>90.3(2)</td>
<td>96.92(13)</td>
</tr>
<tr>
<td>N(7)-Fe-N(5)</td>
<td>97.4(3)</td>
<td>151.40(15)</td>
</tr>
<tr>
<td>N(6)-Fe-N(5)</td>
<td>88.0(2)</td>
<td>96.88(15)</td>
</tr>
<tr>
<td>N(2)-Fe-N(5)</td>
<td>166.7(3)</td>
<td>91.73(13)</td>
</tr>
<tr>
<td>N(7)-Fe-N(3)</td>
<td>95.4(3)</td>
<td>88.38(14)</td>
</tr>
<tr>
<td>N(6)-Fe-N(3)</td>
<td>175.8(3)</td>
<td>89.64(14)</td>
</tr>
<tr>
<td>N(2)-Fe-N(3)</td>
<td>89.6(2)</td>
<td>173.01(14)</td>
</tr>
<tr>
<td>N(5)-Fe-N(3)</td>
<td>91.1(2)</td>
<td>89.89(13)</td>
</tr>
<tr>
<td>N(7)-Fe-N(1)</td>
<td>178.9(3)</td>
<td>77.39(14)</td>
</tr>
<tr>
<td>N(6)-Fe-N(1)</td>
<td>91.9(2)</td>
<td>169.94(14)</td>
</tr>
<tr>
<td>N(2)-Fe-N(1)</td>
<td>83.4(2)</td>
<td>78.74(13)</td>
</tr>
<tr>
<td>N(5)-Fe-N(1)</td>
<td>83.5(3)</td>
<td>74.35(14)</td>
</tr>
<tr>
<td>N(3)-Fe-N(1)</td>
<td>83.9(2)</td>
<td>95.16(13)</td>
</tr>
</tbody>
</table>

\(^a\) Numbers in parentheses are standard uncertainties in the last significant figures. Atoms are labeled as indicated in Figures A5 and A6.
A.3 Results and Discussion

A.3.1 Synthesis of Tripodal Ligands and Iron(II) Complexes

Two tetradentate tripodal ligands (L1 and L2), derivatives of tpa and Me3ntb; where tpa = tris (pyridylmethyl)amine, Me3ntb = tris(2-benzimidazolylmethyl)amine; have been synthesized to provide a systematic variation on the ligand. The structures of the ligands are shown in Scheme A1, together with their abbreviations.


![Scheme A1: Structures of the Tripodal Ligands](image)

Three steps were required for the synthesis of each ligand (Scheme A2 and A3). In general, two synthetic routes for each ligand (L1 and L2) may be considered. The reaction sequences of two different kinds of reactions, substitution and condensation, resulted in dramatically different outcomes. The synthetic route for L1 was utilized by condensation prior to substitution. However, the opposite pathway in which substitution preceded condensation was used in preparing L2. In fact, L2 is a new ligand, and it is worth noting that while L1 and its MnII complex were previously reported, but no experimental details were given.121

Other routes for the synthesis of L1 and L2 were also considered and executed (Scheme A4 and A5). For both routes, the first step could result in reasonable yields, but only low yields could be obtained in the second step.
Scheme A2. Synthetic Routes for L1.

(i) 7 M HCl, reflux, 3 d; (ii) 2 equiv of 2-(chloromethyl)pyridine hydrochloride, NEt₃, 0 → 20 °C, 3 d; (iii) KOH, MeI, 20 °C, 1 h


(i) KOH, K₂CO₃, 0 → 80 °C, 18 h; (ii) 2 equiv of 1,2-diaminobenzene, 6 M HCl, reflux, 3 d; (iii) KOH, MeI, 20 °C, 1 h

Scheme A4. Other Synthetic Route for L1.

(i) NaOH, 20 °C, 5 d; (ii) 1,2-diaminobenzene, 6 M HCl, reflux, 3 d, 2% yield; (iii) KOH, MeI, 20 °C, 1 h
Scheme A5. Other Synthetic Route for \( \textbf{L2} \).

(i) ethylene glycol, 180 °C, 1 d; (ii) 2-(chloromethyl)pyridine hydrochloride, K₂CO₃, 20 °C, 3 d; c) KOH, MeI, 20 °C, 1 h

The Fe\(^{II} \) complexes, [Fe(L₁)(OTf)₂] and [Fe(L₂)(OTf)₂], were synthesized by mixing Fe(OTf)₂·2MeCN with \( \textbf{L1} \) and \( \textbf{L2} \) in THF at ambient temperature, respectively. The complexes were isolated as microcrystalline solids, and characterized by \(^1\)H NMR and UV–Vis spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray diffraction. The solid state structures of [Fe(L₁)(NCMe)₂](OTf)₂ and [Fe(L₂)(NCMe)₂](OTf)₂, obtained from dissolving of [Fe(L₁)(OTf)₂] and [Fe(L₂)(OTf)₂] in MeCN, were crystallographically determined. Each Fe\(^{II} \) ion exhibits a FeN₆ coordination environment with four nitrogen atoms from tetradentate ligand, \( \textbf{L1} \) or \( \textbf{L2} \), and two nitrogen atoms belonging to two MeCN to yield octahedral complexes.

\[ \text{A.3.2 Spectroscopic Characterization} \]

\[ \text{of Iron(II) Complexes} \]

The \(^1\)H NMR spectrum of [Fe(tpa)(OTf)₂] in CD₃CN at room temperature exhibits features of a diamagnetic species, demonstrating that the Fe\(^{II} \) center in [Fe(tpa)(NCCD₃)₂]²⁺ is low spin, \( S = 0 \) (Figure A2, Table A4). Unlike the low-spin complex [Fe(tpa)(NCCD₃)₂]²⁺, complexes [Fe(L₁)(NCCD₃)₂]²⁺ and [Fe(L₂)(NCCD₃)₂]²⁺ have \(^1\)H NMR spectra typical of a high-spin Fe\(^{II} \) complexes with peaks paramagnetically shifted over the range of −10 to +120 ppm (Figure A2, Table A4). These peaks can be assigned by comparison to the spectra of other high-spin complexes, [Fe(tpa)(OTf)₂] in CDCl₃ and [Fe(Me₃ntb)(NCCD₃)₂](OTf)₂ in the literature.\(^{124} \) Thus, the replacement of
even one of the pyridyl substituents in the tripodal ligand with a benzimidazolyl substituent is sufficient to change the Fe$^{II}$ center from low spin to high spin in the [Fe$^{II}(L)(NCCH_3)_2$]$^{2+}$ series at ambient temperature.

Figure A1. $^1$H NMR spectrum of [Fe(tpa)(NCMe)$_2$]$^{2+}$ in CD$_3$CN at room temperature.

Considering the results from $^1$H NMR spectroscopy (narrower range, similar to [Fe(tpa)(OTf)$_2$]), the high-spin complex, [Fe(L1)(NCMe)$_2$](OTf)$_2$, could be able to transform to a low-spin Fe$^{II}$ complex at lower temperature. Therefore, [Fe(L1)(NCCD$_3$)$_2$](OTf)$_2$ was studied by variable temperature $^1$H NMR spectroscopy in the temperature range of −40 to +80 °C (Figure A3). The spectra show that the range of resonances expanded from 20 to 85 ppm with increasing temperature from −40 to +50 °C and becomes narrower again above +50 °C. Therefore, the variable temperature NMR experiment shows that [Fe(L1)(NCCD$_3$)$_2$](OTf)$_2$ in acetonitrile exhibits a mixture of high- and low-spin species in the temperature range of −40 to +50 °C, and transforms to pure high-spin at a temperature of ca. 50 °C. For comparison, [Fe(L2)(NCCD$_3$)$_2$](OTf)$_2$
was acquired by variable temperature $^1$H NMR spectroscopy in the same temperature range (Figure A4). The spectra show that the range of resonances shrinks from 160 to 100 ppm with increasing temperature from $-40$ to $+80$ °C. Unlike expansion and then shrinkage for $[\text{Fe(L1)}(\text{NCCD}_3)_2]$(OTf)$_2$, only shrinking $^1$H NMR spectra of $[\text{Fe(L2)}(\text{NCCD}_3)_2]$(OTf)$_2$ was observed, indicating that $[\text{Fe(L2)}(\text{NCCD}_3)_2]$(OTf)$_2$ remains high-spin in this temperature range.

**Table A4.** $^1$H chemical shifts, $\delta$ (ppm), of the Fe$^{II}$ complexes $[\text{Fe(tpa)}(\text{NCMe})_2]^{2+}$, $[\text{Fe(L1)}(\text{NCMe})_2]^{2+}$, $[\text{Fe(L2)}(\text{NCMe})_2]^{2+}$, and $[\text{Fe(Me}_3\text{ntb)}(\text{NCMe})]^{2+}$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\alpha$-H 6-H$_{py}$</th>
<th>NCH$_2$</th>
<th>$\beta$-H, $\beta'$-H 3-H$<em>{py}$, 5-H$</em>{py}$</th>
<th>$\gamma$-H 4-H$_{py}$</th>
<th>NCH$_3$</th>
<th>Ar H 7-H$_{bzim}$</th>
<th>NCH$_3$</th>
<th>Ar H 5-H$_{bzim}$</th>
<th>Ar H 6-H$_{bzim}$</th>
<th>Ar H 4-H$_{bzim}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(tpa)}(\text{NCCD}_3)_2]^{2+}$</td>
<td>3H, 11.2</td>
<td>6H, 6.40</td>
<td>6H, 8.52, 8.47</td>
<td>3H, 7.42</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
</tr>
<tr>
<td>$[\text{Fe(tpa)}$(OTf)$_2$]^{b}$</td>
<td>n. o. $^c$</td>
<td>6H, 64.8</td>
<td>6H, 52.7, 51.4</td>
<td>3H, 10.3</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
<td>n. o.</td>
</tr>
<tr>
<td>$[\text{Fe(L1)}(\text{NCCD}_3)_2]^{2+}$</td>
<td>2H, 86.8</td>
<td>4H, 71.2</td>
<td>4H, 48.2, 44.3</td>
<td>2H, −8.1</td>
<td>2H, 115.8</td>
<td>2H, 96.8</td>
<td>2H, 54.1</td>
<td>2H, 52.6</td>
<td>2H, −12.8</td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe(L2)}(\text{NCCD}_3)_2]^{2+}$</td>
<td>1H, 115.8</td>
<td>2H, 96.8</td>
<td>2H, 54.1, 52.6</td>
<td>2H, −12.8</td>
<td>1H, 59.5</td>
<td>1H, 25.8</td>
<td>3H, 16.1</td>
<td>1H, 3.8</td>
<td>1H, 2.2</td>
<td>1H, −5.3</td>
</tr>
<tr>
<td>$[\text{Fe(L1)}(\text{NCCD}_3)_2]^{2+}$</td>
<td>4H, 75.8, 71.2</td>
<td>2H, 28.7</td>
<td>6H, 19.6</td>
<td>2H, 3.2</td>
<td>2H, 13</td>
<td>2H, 3.2</td>
<td>2H, 1.3</td>
<td>2H, −4.0</td>
<td>2H, −4.0</td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe(L2)}(\text{NCCD}_3)_2]^{2+}$</td>
<td>6H, 83.2</td>
<td>3H, 27.1</td>
<td>9H, 18.5</td>
<td>3H, 4.3</td>
<td>3H, 1.7</td>
<td>3H, 1.7</td>
<td>(ca. 3.5)$^d$</td>
<td>(ca. 3.5)$^d$</td>
<td>(ca. 3.5)$^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In CD$_3$CN. $^b$ In CDCl$_3$. $^c$ n. o. = not observed. $^d$ This resonance overlaps with the resonance at 4.3 ppm.
Figure A2. $^1$H NMR spectra of [Fe(tpa)(OTf)$_2$] in CDCl$_3$ and [Fe(L1)(NCMe)$_2$]$^{2+}$, [Fe(L2)(NCMe)$_2$]$^{2+}$, and [Fe(Me$_3$ntb)(NCMe)]$^{2+}$ in CD$_3$CN at room temperature.

A.3.3 Crystal Structures of Iron(II) Complexes

The Fe$^{II}$ center in each complex is in a distorted octahedral environment ligated by the two/one pyridine nitrogen(s), one/two benzoimidazole nitrogen(s) and one amine nitrogen of the tripodal ligand, and two acetonitrile nitrogens (Figures A5 and A6). Although [Fe(L1)(NCMe)$_2$](OTf)$_2$ and [Fe(L2)(NCMe)$_2$](OTf)$_2$ have similar coordination geometries, the Fe–N bond lengths and bond angles differ greatly between these two complexes, reflecting the difference in spin state (Tables A2 and A3). For example, although Fe–N$_{amine}$ distance in both complexes is longer than the other Fe–N
bonds, the Fe–N<sub>amine</sub> distance of 2.033(4) Å in [Fe(L1)(NCMe)<sub>2</sub>](OTf)<sub>2</sub> is significantly shorter than the Fe–N<sub>amine</sub> distance of 2.303(5) Å in [Fe(L2)(NCMe)<sub>2</sub>](OTf)<sub>2</sub>.

Likewise, the Fe–N<sub>py</sub>, Fe–N<sub>hzim</sub>, and Fe–N<sub>MeCN</sub> bond lengths of [Fe(L1)(NCMe)<sub>2</sub>](OTf)<sub>2</sub> are 0.20–0.21 Å, 0.12–0.15 Å, and 0.16–0.27 Å shorter than the corresponding Fe–N distances in [Fe(L2)(NCMe)<sub>2</sub>](OTf)<sub>2</sub>, respectively. The Fe–N distances reflect different chemical nature of the donor atoms. With the similar Fe–N bond lengths in [Fe(L1)(NCMe)<sub>2</sub>](OTf)<sub>2</sub>, this complex is expected to be a low-spin Fe<sup>II</sup>.
complex. Moreover, the average Fe–N\textsubscript{py} distance of 1.97 Å found in [Fe(L\textsf{1})(NCMe)\textsubscript{2}](OTf)\textsubscript{2} is comparable to those typically found in low-spin Fe\textsuperscript{II} complexes, such as [Fe(phen)\textsubscript{3}]\textsuperscript{2+} (1.97 Å),\textsuperscript{125} [Fe(bpy)\textsubscript{3}]\textsuperscript{2+} (1.96 Å),\textsuperscript{126} [Fe(tpa)(NCMe)\textsubscript{2}]\textsuperscript{2+} (1.95 Å).\textsuperscript{127} On the contrary, with a noticeably longer Fe–N\textsubscript{amine} bond length than Fe–N\textsubscript{bzim}, Fe–N\textsubscript{MeCN}, and Fe–N\textsubscript{py} (0.10 to 0.18 Å), [Fe(L\textsf{2})(NCMe)\textsubscript{2}](OTf)\textsubscript{2} is expected to be a high-spin Fe\textsuperscript{II} complex.

\textbf{Figure A4.} VT\textsuperscript{-1}H NMR spectra of [Fe(L\textsf{2})(OTf)\textsubscript{2}] in CD\textsubscript{3}CN in the temperature range of −40 to +80 °C.
Figure A5. Molecular structure of the complex cation of $[\text{Fe}(\text{L1})(\text{NCMe})_2](\text{OTf})_2$; displacement ellipsoids are drawn at 50% probability level; hydrogen atoms have been omitted for clarity.

Figure A6. Molecular structure of the complex cation of $[\text{Fe}(\text{L2})(\text{NCMe})_2](\text{OTf})_2$; displacement ellipsoids are drawn at 50% probability level; hydrogen atoms have been omitted for clarity.
A.3.4 Generation and Characterization of Oxoiron(IV) Complexes

Addition of 3 equiv of \( m \)-chloroperbenzoic acid (\( m \)CPBA) to a solution containing 1 mM of \([\text{Fe}(\text{L1})(\text{OTf})_2]\) and \([\text{Fe}(\text{L2})(\text{OTf})_2]\) immediately gave pale greenish solution with absorption bands at 733 nm (\( \varepsilon \approx 220 \text{ M}^{-1} \cdot \text{cm}^{-1} \)) and 747 nm (\( \varepsilon \approx 200 \text{ M}^{-1} \cdot \text{cm}^{-1} \)), respectively, in CH\(_3\)CN at \(-40^\circ\text{C}\) (Figures A7 and A8). Compared to \([\text{Fe}(\text{tpa})(\text{OTf})_2]\) under the same reaction conditions, the intermediates were unstable and decayed faster (decay began at 10 min and 1 min for \([\text{Fe}(\text{L1})(\text{OTf})_2]\) and \([\text{Fe}(\text{L2})(\text{OTf})_2]\), respectively). Due to the fast decay of Fe\(^{IV}=O\) intermediates, growing single crystals of both intermediates for characterization is extremely challenging. Electrospray ionization mass spectrometer would be the suitable instrument for analyzing this type of species. However, when subjecting the solutions generated from Fe\(^{II} + m \)CPBA into mass spectrometer, no ion peaks represented Fe\(^{IV}=O\) could be observed, which may be due to acceleration of decomposition of Fe\(^{IV}=O\) by \( m \)CBA (hydroxylation of the aromatic ring of \( m \)CBA to form the corresponding Fe\(^{III}\) product). \(^{128}\) Hence, using other oxidants, which may prevent activation of C–H bonds, could help us obtain the desired results. As described in the Experimental Section, peracetic acid could also be used for preparing the Fe\(^{IV}=O\) intermediate with slightly lower yield. Therefore, in order to clarify the identification of peaks in mass spectra, peracetic acid was used instead of \( m \)CPBA. The ESI(+)-MS spectrum of \([\text{Fe}(\text{L2})(\text{OTf})_2]\) exhibits overlapping ion peaks, whose mass and isotope distribution patterns correspond to \([\text{Fe}^{IV}(\text{O})(\text{L2})(\text{OTf})]^+\) and \([\text{Fe}^{III}(\text{OH})(\text{L2})(\text{OTf})]^+\) at \( m/z = 617.9 \) and 618.9, respectively in addition with other decay product, Fe\(^{III}\) species, \( i.e. \ m/z = 1276.7, \{2 \ [\text{Fe}(\text{L2})] + 2 \text{ OTf} + \text{OAc} + \text{O}\}^+\). The \([\text{Fe}^{III}(\text{OH})(\text{L2})(\text{OTf})]^+\) likely forms from the decomposition of \([\text{Fe}^{IV}(\text{O})(\text{L2})(\text{OTf})]^+\).
Figure A7. UV–Vis spectra of 1 mM of [Fe(L1)(NCMe)_2]^{2+} (yellow) and [Fe^{IV}(O)(L1)(NCMe)_2]^{2+} (green) in CH_3CN at −40 °C.

Figure A8. UV–Vis spectra of 1 mM of [Fe(L2)(NCMe)_2]^{2+} (yellow) and [Fe^{IV}(O)(L2)(NCMe)_2]^{2+} (green) in CH_3CN at −40 °C.
A.4 Conclusion

Two Fe$^{II}$ complexes having tripodal tetradentate ligands, $N$-[1-(1-Methylbenzimidazol-2-yl)methyl]-$N,N$-bis[(pyridin-2-yl)methyl]amine (L1) or $N,N$-Bis[(1-methylbenzimidazol-2-yl)methyl]-$N$-[(pyridin-2-yl)methyl]amine (L2) have been prepared and characterized in both solution and solid states. Spectroscopic analyses suggest that the spin states of [Fe(L1)(NCMe)$_2$]$^{2+}$ and [Fe(L2)(NCMe)$_2$]$^{2+}$ are high-spin (S = 2) in solution, but low-spin (S = 0) and high-spin in the solid state, respectively. [Fe(L2)(NCMe)$_2$]$^{2+}$ in acetonitrile exhibits spin equilibrium between low-spin and high-spin over the temperature range from −40 to 50 °C. This study provides the structural basis that replacing pyridyl with benzimidazolyl substituents could change the spin state and also tune the reactivity of Fe centers, which is demonstrated by the formation and stability of Fe$^{IV}$=O species.
REFERENCES


116. Abbreviations: TfO– (= CF₃SO₃–), trifluoromethanesulfonate or triflate anion.


124. Although the ¹H NMR spectrum of [Fe(Me₃ntb)(NCCD₃)₂](OTf)₂ does not provide a useful information in the literature, we have re-done the ¹H NMR experiment by using proper parameters to obtain a better spectrum.


129. Haynes, W. M. *CRC Handbook of Chemistry and Physics*, 92nd ed.; CRC Press: